GEORGIA INSTITUTE OF TECHNOLOGY — OFFICE OF CONTRACT ADMINISTRATION

PROJECT ADMINISTRATION DATA SHEET

[x] ORIGINAL [ ] REVISION NO. _____

Project No. E-20-H01 DATE 5/12/82

Project Director: Dr. F. G. Pohland School/Lab CE

Sponsor: Sanifoam, Inc.

Type Agreement: Standard Research Agreement No. E-20-H01

Award Period: From 5/5/82 To ~~5/4/83~~ 11/4/83 (Performance) ~~5/4/83~~ 11/4/83 (Reports)

Sponsor Amount: $22,360 (Advance payment of $5,000) Contracted through: GTRI/GIT

Cost Sharing: _____

Title: The Use of Plastic Foam as a Cover Material During Landfilling of Solid Wastes

ADMINISTRATIVE DATA OCA Contact Faith Costello

1) Sponsor Technical Contact:

Mr. Fritz Kramer
President
Sanifoam, Inc.
1370 Logan Ave., Suite D
Costa Mesa, CA 92626

2) Sponsor Admin/Contractual Matters:

Mr. Fritz Kramer
President
Sanifoam, Inc.
1370 Logan Ave., Suite D
Costa Mesa, CA 92626

Defense Priority Rating: N/A Security Classification: N/A

RESTRICTIONS

See Attached N/A Supplemental Information Sheet for Additional Requirements.

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Equipment: Title vests with sponsor

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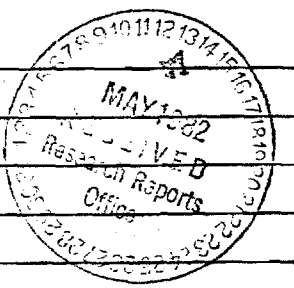

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GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 1/12/84

Project No. E-20-H01 School CE

Includes Subproject No.(s)

Project Director(s) Dr. F. G. Pohland GTRI

Sponsor Sanifoam, Inc.

Title The Use Of Plastic Foam As A Cover Material During Landfilling of Solid Wastes

Effective Completion Date: 12/4/83 (Performance) 12/4/83 (Reports)

Grant/Contract Closeout Actions Remaining:

- [ ] None
- [X] Final Invoice
- [ ] Closing Documents
- [ ] Final Report of Inventions
- [ ] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other

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GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
CIVIL ENGINEERING

October 1, 1982

TELEPHONE:
(404) 894-2265

Mr. Fritz Kramer, President
Sanifoam, Inc.
Suite D
Costa Mesa, CA 92626

Re: "The Use of Plastic Foam as a Cover Material During Landfilling of Solid Wastes" (E-20-H01)

Dear Mr. Kramer:

In accordance with the goals of the subject research project, two simulated landfill cells have been constructed to provide an opportunity to assess the relative suitability and/or ptoential of using Sanifoam plastic foam as a cover material during landfilling of solid wastes. These two cells have been operated with a 2-inch layer of foam placed between shredded municipal refuse exposed to single pass and recycled moisture additions. Hence, the single pass cell simulates conventional landfilling practice; the recycle cell simulates conditions where leachate is contained, collected and recycled, using the landfill as lined, in situ leachate treatment system.

Each cell has been sealed and initially brought to apparent field capacity with distilled water. Thereafter, moisture has been added corresponding to rainfall incidents in the Atlanta area with accumulated leachate being collected, analyzed and recycled daily in the recycle unit and collected, analyzed and removed to storage after each rainfall event for the single pass unit. Leachate (and gas) analyses are being performed to determine stage of landfill decomposition and leachate and gas characteristics. Data collected since July 17, 1982 indicate that acid fermentation has begun in both cells with associated high pollutant concentrations (BOD, TOC, COD, volatile acids) and low pH in the leachate without significant gas production being detected to date. These analyses reflect a very typical condition of a landfill undergoing the early stages of decomposition.

Associated with the routine operation and analyses has been a special consideration of the behavior of the foam with regard to possible contributions to the leachate and effects on rates of stabilization and gas generation. To this end, several analytical procedures have been explored and applied to the analysis of both simple and complex aqueous samples. The former samples were acquired from a simple distilled water and organic acid (acetic acid) rinsing of samples of foam obtained during construction of the experimental cells. The latter samples were obtained from leachates generated from the two test cells with time.

Analytical methods used included the chromotrophic acid coloremetric technique, a gas chromatographic technique, and a GC-MS technique utilizing aqueous samples in all cases. Since no standard technique for formaldehyde has been established for aqueous waste samples such as leachate, these were considered to be a fair representation of potentially applicable techniques. However, all were found to have limitations particularly when applied for analysis of the leachate samples. The colorimetric technique suffered by interferences with other compounds known to be present in the leachate that interfered with the formation and/or intensity of color, the gas chromatographic technique used did not provide the degree of peak separation considered requisite for reliable analyses, and the GC-MS analysis, although most specific with regard to determining the presence or absence of formaldehyde, could not detect concentrations below about 100 ppm. Therefore, detection of formaldehyde in complex leachate samples, although indicating less than 100 ppm, could not be specifically confirmed primarily due to the abundance of other reactive constituents in the leachate samples, both with and without the foam as a basic ingredient.

In spite of these difficulties, examination of these techniques and comparison of corresponding results on the leachate samples to date, coupled with the results of rinsing tests on the foam samples where many of these complex interferences were not present or certainly minimized, leads to the conclusion that release and persistence of formaldehyde originating from the foam is comparatively small and relatively insignificant with regard to its contribution to potential environmental impacts. This conclusion becomes even more justified when the known chemical and biological reactivity of formaldehyde with respect to its rapid degradation both in the aqueous leachate medium and solid waste mass are considered. Moreover, the time required to reach leaching conditions sufficient to allow migration, the slow progress of leachate movement from most conventional landfill sites, and the opportunity for high dilution by infiltration during leaching processes and/or in the groundwater system if released tend to further minimize this impact and preclude the likelihood of detection in water supply systems. Therefore, in the absence of data to the contrary, the use of the foam as a cover in landfill practice appears to be a viable operational alternative.

Confirmation of the results and/or conclusions to date are being provided by continuing studies on leachates generated within the test cells as well as from other sources. In addition, continuing effort is being directed at resolving some of the analytical difficulties and determining whether the foam will have any effect on leachate quality and/or gas generation as methane fermentation is established. The results of these efforts will be reported at the end of the next project phase.

I trust that this preliminary information will serve to update you with regard to research progress on the Sanifoam project at Georgia Tech. As

mentioned in our previous discussions, we would invite you to inspect our research facilities and discuss these results in more detail.

Best regards.

Sincerely

Frederick G. Pohland
Professor of Civil Engineering

FGP/hb

cc: Dr. J. E. Fitzgerald, CE
Ms. Faith Costello, OCA

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83-101

INTERIM PROGRESS REPORT

PROJECT E-20-H01

THE USE OF PLASTIC FOAM AS AN INTERMEDIATE COVER MATERIAL DURING LANDFILLING OF SOLID WASTES

SUBMITTED TO

SANIFOAM, INC.
COSTA MESA, CALIFORNIA

BY

FREDERICK G. POHLAND
SCHOOL OF CIVIL ENGINEERING
GEORGIA INSTITUTE OF TECHNOLOGY

JANUARY 1983

GEORGIA INSTITUTE OF TECHNOLOGY
A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA
SCHOOL OF CIVIL ENGINEERING
ATLANTA, GEORGIA 30332

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ABSTRACT

This research project was initiated to assess the relative suitability and/or potential of using SaniFoam plastic foam as an intermediate cover material during landfilling of solid wastes. To accomplish this aim, the research efforts to date have been directed toward: development of an analytical method for the specific determination and quantification of formaldehyde in leachates; start-up and operation of single-pass and recycle simulated landfill cells to assess the potential impact of SaniFoam plastic foam on the landfill environment; start-up and operation of simulated landfill cells with and without foam to determine the relative contribution of formaldehyde to leachate from the foam as compared with other constituents present in solid wastes; and, evaluation of the extractability of formaldehyde from the foam using immersion and percolation tests.

The results of these efforts indicate that, although there is not presently a standard analytical method for determination of formaldehyde in complex aqueous solutions, the derivatization of formaldehyde as 2, 4-dinitrophenylhydrazone (DNPH) and subsequent extraction, concentration and analysis by gas chromatography (GC) is a viable method for the quantification of trace amounts of formaldehyde in leachate. In addition, the simulated landfill tests have indicated that, in the presence of leachate typical of that from landfills undergoing early stages of microbially mediated decomposition, concentrations of formaldehyde ranged from 3 to 15 mg/l. However, formaldehyde in the leachate could be attributed to other constituents present in the solid waste and could also be extracted from the foam by the percolation of water through the foam. Therefore, investigations are continuing to complete and verify these initial observations.

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INTRODUCTION

This progress report summarizes the results to date on the assessment of the relative suitability and/or potential applicability of SaniFoam plastic foam as an intermediate cover material during landfilling of solid wastes. Efforts have been focused on four main areas including: development of a specific method for quantification of formaldehyde in leachate; assessment of potential impact and fate of the foam within the landfill environment, particularly in association with natural processes of stabilization and gas production; determination of the relative contribution of formaldehyde to leachate from the foam as compared with other constituents present in the solid waste; and, potential extractability of formaldehyde from the foam.

Assessment of the impact of the foam on the landfill environment required the periodic analysis of leachate samples for various parameters. Most of these analyses have been derived from methods used in wastewater monitoring and their application for the analyses of leachate presented few analytical difficulties. However, this was not the case for the analyses of trace amounts of specific organic compounds (e.g., formaldehyde), since the leachate itself as well as constituents from the foam interfered with the isolation and quantification of such compounds. Although there are established analytical techniques for the measurement of formaldehyde, these are primarily used to measure relatively high concentrations in solutions of known composition (e.g., quality control in manufacturing processes) or for monitoring formaldehyde concentrations in ambient air and/or occupational environments.[1] Therefore, since little information was available to determine the relative accuracy, precision and sensitivity of various methods in complex aqueous samples, efforts were initiated to assess the applicability of selected methods for the analysis of

formaldehyde in leachate and to subsequently select and/or develop an analytical technique that could be used with reliability to specifically detect and quantify trace amounts of formaldehyde in the leachates generated during these studies.

Landfilled solid wastes undergo a sequence of microbially mediated conversion processes which both stabilize the waste constituents in situ and transfer the conversion products to the leachate emanating from the site. Therefore, it could be anticipated that foam used for intermediate cover would be exposed to a variety of environmental conditions. Normally the processes causing these conditions occur over extended periods of time, thereby making analysis and interpretation difficult. However, by collecting and recycling the leachate through the waste, these processes can be accelerated and made to occur in a more predictable fashion and within a more manageable time frame. Consequently, this leachate recycle strategy, compared with single-pass operation, was used to accelerate exposure of the foam to various environmental conditions and to enable the assessment of the impact of the foam on the landfill environment.

Since formaldehyde is widely used in the production and manufacturing of many products, it could be anticipated that such materials would become a potential source of formaldehyde in the simulated landfills. Consequently, to determine the possible contribution of the various constituents of typical municipal solid waste to the total formaldehyde present in leachate, leachates generated by the simulated landfill cells containing municipal solid waste in the presence and absence of foam were evaluated for formaldehyde. To augment this effort and to determine the leaching characteristics of the foam when exposed to various environmental and moisture conditions, tests were also conducted to determine if formaldehyde

could be extracted from the foam by immersion in various simpler aqueous solutions together with percolation of distilled water through a foam layer.

The research efforts in each of these areas, in conjunction with the results obtained to date, are presented and discussed in the subsequent sections of this report.

ANALYTICAL METHODS

Leachate Characterization

Assessment of the impact of SaniFoam plastic foam on the simulated landfill cells necessitated the periodic collection and analysis of leachate samples to characterize the leachate and determine the stage of landfill decomposition. The parameters monitored and the analytical methods used are summarized in Table 1.

Formaldehyde Analysis

In addition to the routine methods used for characterization of the leachate, a search for a specific analysis for formaldehyde in complex aqueous solutions (e.g., leachate) was undertaken. Although there exists several established analytical methods for the measurement of formaldehyde in air,[1,2] little research has been performed to determine aldehydes in aqueous solutions and no standard analytical method has been developed for the measurement of formaldehyde in complex aqueous waste samples such as leachates. Therefore, several analytical methods were evaluated for the analysis of formaldehydes in leachate samples. These included: i) the chromotropic acid colorimetric technique; ii) a direct aqueous injection, packed column Gas Chromatographic (GC) technique; and, iii) a direct aqueous injection, capillary column Gas Chromatographic-Mass Spectroscopic (GC-MS) technique. All of these methods, however, were found to have limitations (Table 2) which ultimately restricted their use for the determination of trace amounts of formaldehyde in leachate samples.

TABLE 1. ANALYTICAL METHODS AND INSTRUMENTATION

Parameter	Method
pH	Standard Methods*; Fisher Accumet pH/mV meter, Model 610
Oxidation-Reduction Potential (ORP)	Standard Methods*; Fisher Accumet pH/mV meter, Model 610
Conductivity	Standard Methods*; YSI Conductivity Bridge, Model 31
Total Alkalinity	Standard Methods*
Total Organic Carbon (TOC)	Standard Methods*; Beckman Total Organic Carbon Analyzer, Model 915
5-Day Biochemical Oxygen Demand (BOD_5)	Standard Methods*
Chemical Oxygen Demand (COD)	Standard Methods*
Volatile Fatty Acids	Direct aqueous injection; Hewlett Packard GC 5710A, packed column - 2 m x 2 mm I.D., Carbopack B 60-80 mesh, modified with 1% carbowax 20 M and 1.5% phosphoric acid
Sulfides	Orion silver/sulfide electrode, Model 94-16 with Fisher Accumet pH/mV meter, Model 610
Metals	Standard Methods*; Perkin Elmer Atomic Absorption Spectrophotometer, Model 303
Carbon, Hydrogen and Nitrogen	Standard Methods*; F&M Scientific Corp. Carbon-Nitrogen-Hydrogen Analyzer, Model 185
Gas Composition	Standard Methods*; Fisher Gas Partitioner

*Standard Methods for the Examination of Water and Wastewater, 15th Ed., APHA, AWWA, WPCF (1981)

TABLE 2. LIMITATIONS OF ANALYTICAL METHODS FOR THE DETERMINATION OF FORMALDEHYDE IN COMPLEX AQUEOUS SOLUTIONS

Method*	Limitations
Chromotropic Acid, Colorimetric Method	Although this method has been effectively used to detect low concentrations of formaldehyde with good accuracy, the reliability of the method decreases when used with complex mixtures (e.g., leachate) due to the presence of other compounds in the solution that can interfere with the formation and/or intensity of color. Compounds which can cause interference with this method include, acetaldehyde, acrolein, beta-hydroxypropionaldehyde, methyl ethyl ketone and diacetone alcohol. Some of these compounds or others are likely to be present in leachate. In addition, natural color of the leachate masks any color development, thereby further complicating the use of this method.
Direct Aqueous Injection, Gas Chromatographic Technique	Direct aqueous injection GC methods have been used for determination of relatively high concentrations of formaldehyde in simple aqueous solutions. However, this method did not provide for the degree of peak separation considered requisite for reliable analyses with leachate samples.
Direct Aqueous Injection, Gas Chromatography-Mass Spectroscopy (GC-MS) Technique	Although capillary columns and GC-MS are more reliable for determining the presence or absence of formaldehyde, concentration levels below 100 mg/l in aqueous solutions could not be detected.

*Analytical methods and/or experimental conditions for these methods are presented in more detail in Appendix A.

A review of the applicable literature indicated that several investigators[3-5] have successfully used derivatization techniques prior to gas chromatographic (GC) or high pressure liquid chromatographic (HPLC) analysis for the determination of trace amounts of aldehydes and other carbonyl compounds. Mansfield, et al.,[3] successfully used the

formation of 2,4-dinitrophenylhydrazone (DNPH) from the reaction of formaldehyde with 2,4-dinitrophenylhydrazine (DHP) to detect formaldehyde in tobacco smoke. Fung and Grosjean,[4] as well as Selin[5] have similarly used the derivatization to DNPH's to separate and quantify nanogram amounts of carbonyl compounds.

Although none of the investigators have applied these techniques to complex aqueous solutions, use of this derivatization technique appeared feasible for specific determination and quantification of formaldehyde in leachate samples. Consequently, analytical method development efforts were directed in this area to take advantage of the well known reaction of carbonyl compounds with 2,4-dinitrophenylhydrazine (DNP) and subsequent formation of the derivative 2,4-dinitrophenylhydrazone (DNPH) according to the reaction:

$$RR'C{=}O + NH_2NHC_6H_3(NO_2)_2 \text{ ------> } RR'C{=}NNHC_6H_3(NO_2)_2 + H_2O$$

The derivative is extracted from the aqueous solution with an organic solvent which is subsequently separated from the solution, concentrated and then analyzed by GC.

To verify the formation extraction and analysis of the DNPH derivative, DNP reagent was added to 500 ppb formaldehyde standard solutions prepared in "organic free" water and allowed to react at 45°C for two hours. The derivative was then extracted with methylene chloride, concentrated and then analyzed by glass capillary column GC. Further verification of the DNPH formation was provided by GC-MS analysis. The reconstructed ion chromatogram

(RIC) and the mass spectrum of the DNPH are shown in Figures 1 and 2, respectively.

Upon verification of the formation, extraction and analysis of the DNPH derivative, "blank" determinations were performed with the "organic free" water used in these analyses, as well as the distilled water that was added to the single-pass and recycle simulated landfill cells, to ensure that no formaldehyde was initially present in these aqueous samples or introduced during sample manipulation. Results of these analyses indicated absence of DNPH formation and it was, therefore, concluded that formaldehyde was not initially present.

The reproducibility of the analytical procedure was evaluated by analyzing four distilled water samples spiked with formaldehyde to the 500 ppb level. The "internal standard method" (internal standard: hexamethylbenzene) was used for the quantification of the DNPH derivative. The results are presented in Table 3 and indicated that acceptable reproducibility could be achieved.

TABLE 3. REPRODUCIBILITY OF RESULTS FOR THE DERIVATIZATION OF FORMALDEHYDE TO 2,4-DINITROPHENYLHYDRAZONE (DNPH) IN DISTILLED WATER

Sample Identification*	Amount of DNPH Measured**, nanograms	Mean	Standard Deviation	Coefficient of Variation
H-1	50.00			
H-2	50.88			
		58.9	11.2	19.0%
H-3	57.12			
H-4	77.74			

*Samples consisted of 100 ml samples of "organic free" water spiked to 500 ppb with formaldehyde (50 nanograms per sample).
**Internal Standard: hexamethylbenzene.

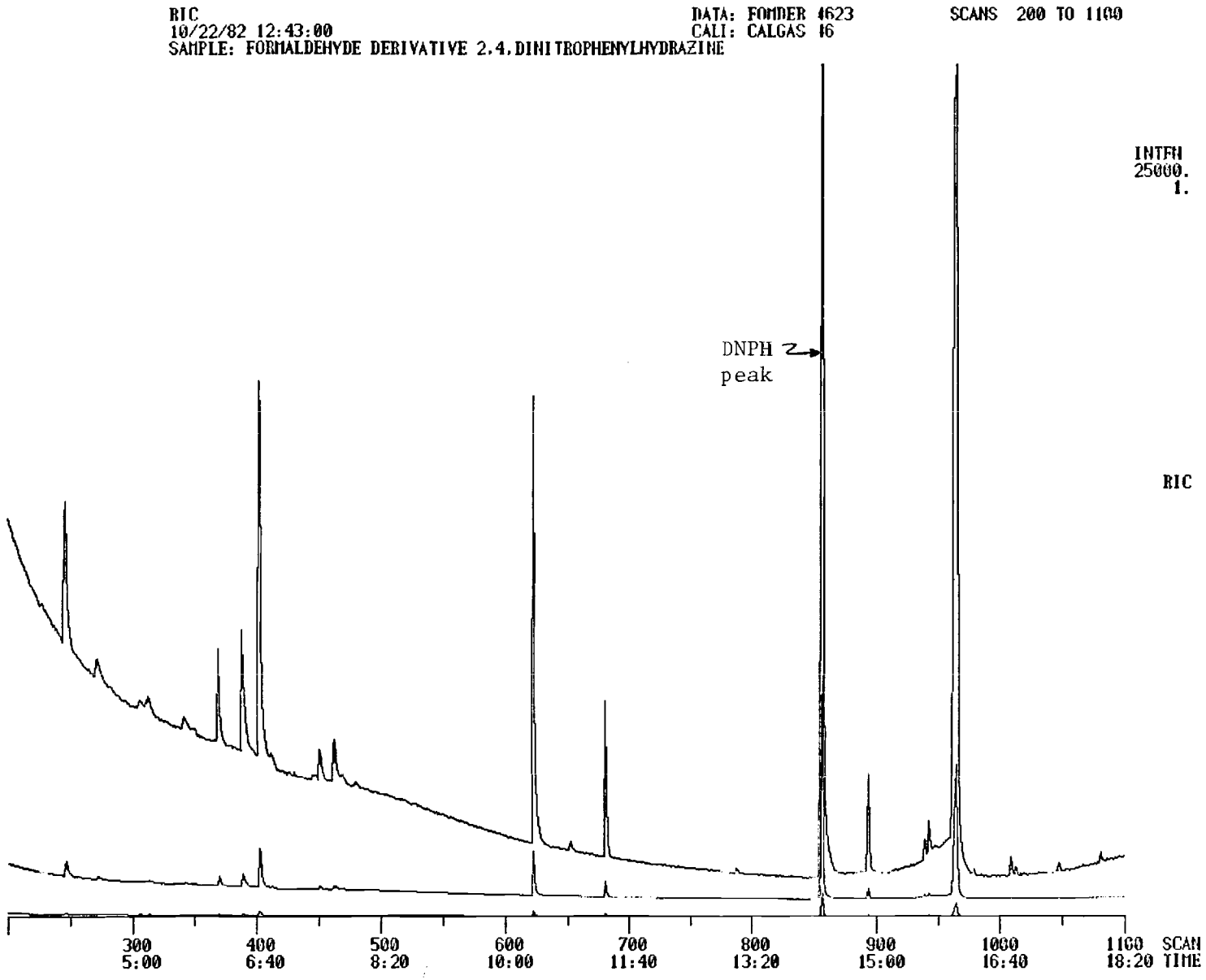

Figure 1. Reconstructed Ion Chromatogram of 2,4-Dinitro phenylhydrazone(DNPH) Derivative.

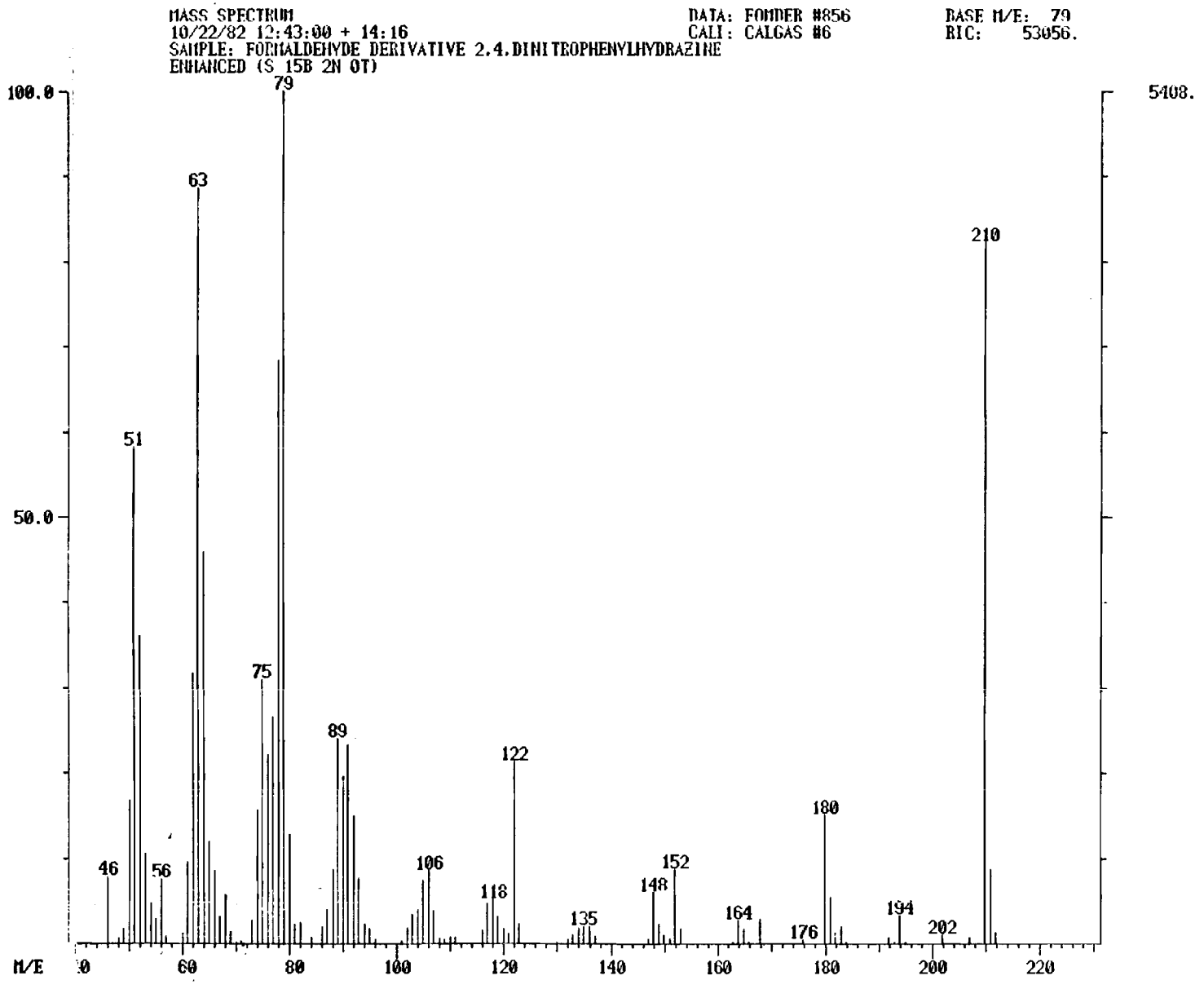

Figure 2. Mass Spectrum of 2,4-Dinitrophenylhydrazone (DNPH).

Following this initial success with standard aqueous solutions, the analytical procedure was applied to leachate samples. Results from these tests revealed that DNPH could also be formed, extracted and concentrated from the leachate samples under investigation. Verification of the DNPH derivative were made by GC-MS analysis (Figures 3 and 4).

Initial tests conducted to determine the reproducibility of the analytical procedure for leachate samples indicated a high variance in results. This was primarily attributed to the fact that external standards (distilled water spiked with formaldehyde to the 500 ppb level) were used for the GC analysis, since the internal standard initially selected (hexamethylbenzene) had a retention time that coincided with that of other co-extracted compounds present in the leachate. Another cause of high variance was attributed to the formation of thick emulsions when extracting leachate samples with methylene chloride. Elimination of these emulsions was attempted by the addition of a saturated calcium chloride solution in order to raise the ionic strength of the sample, but no beneficial effects were observed. Alternatively, a steam distillation solvent extraction method was evaluated in order to extract the DNPH from the leachate. However, very poor recovery of the DNPH was obtained. Therefore, to further improve on the reproducibility of the analytical method, a modification of the reaction procedure was introduced by continuously mixing the sample upon the addition of the reagent in the presence of the organic solvent. The addition of the solvent directly to the sample while reaction occurs could allow partitioning of the DNPH into the solvent phase immediately upon formation.

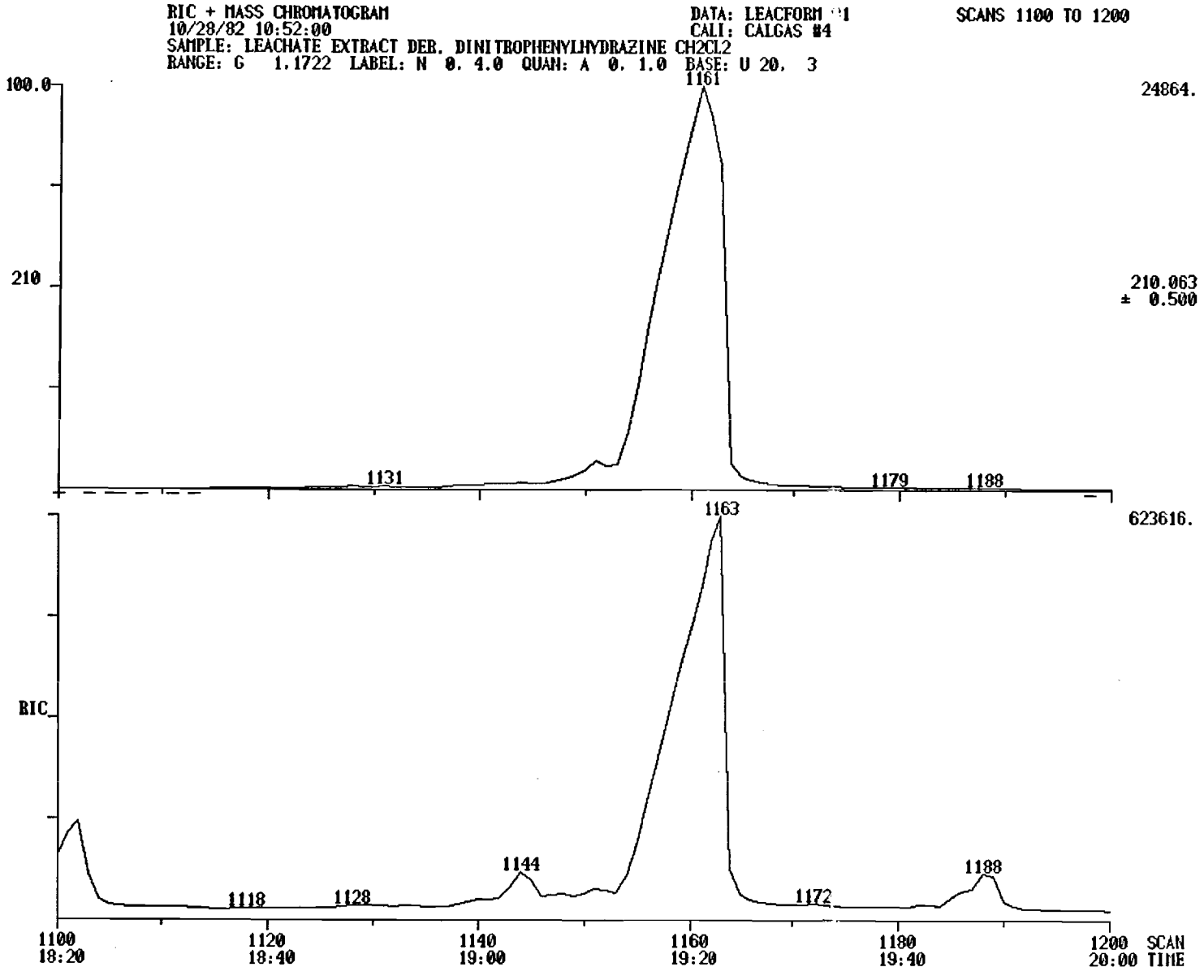

Figure 3. Selected Ion Plot of 2,4-Dinitrophenylhydrazone (DNPH) Extracted from Leachate.

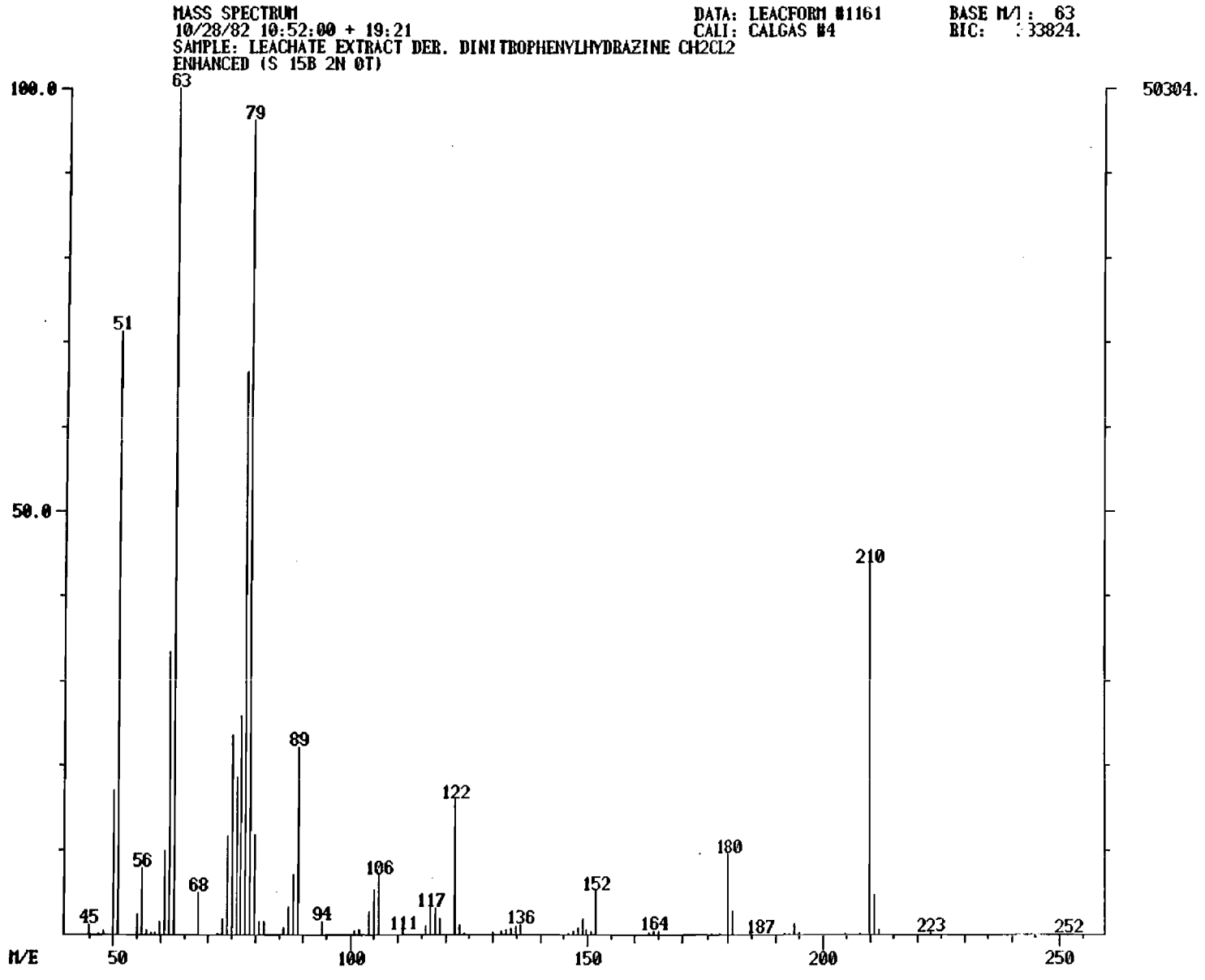

Figure 4. Mass Spectrum of 2,4-Dinitrophenylhydrazone (DNPH) Extracted from Leachate.

To enable the use of the "internal standard method" for the quantitation of the DNPH derivative in leachate samples, decachlorobiphenyl (DCBP) was selected as an internal standard. DCBP was found to be suitable for use with leachate samples since its retention time did not coincide with that of other compounds present in the leachate. Use of DCBP as an internal standard has resulted in an improved reproducibility of results with both distilled water samples "spiked" with formaldehyde and leachate samples (Table 4).

The analytical method that has been developed to date and is currently being used for the determination of trace amounts of formaldehyde in leachate is described in detail in Appendix B. Efforts are continuing to resolve difficulties with variance in results and the formation of emulsions with leachate samples.

TABLE 4. REPRODUCIBILITY OF RESULTS FOR THE DERIVATIZATION OF FORMALDEHYDE TO 2,4-DINITROPHENYLHYDRAZONE (DNPH) IN DISTILLED WATER AND LEACHATE SAMPLES

Sample Identification	Amount of DNPH Measured*, nanograms	Mean	Standard Deviation	Coefficient of Variation, %	Comment
D-1	60.96				
D-2	56.86	56.05	3.17	5.66	Distilled water "spiked" to 500 ppb with formaldehyde.
D-3	54.15				
D-4	52.21				
F-1	118.30				
F-2	117.40	117.85	0.45	0.38	Leachate samples from bench-scale simulated landfill cell containing foam.
C-7	543.65				
C-8	426.68	485.17	58.48	12.05	Leachate samples from single-pass simulated landfill cell.

*Internal Standard: Decachlorobiphenyl

SIMULATED LANDFILL CELLS

Preparation and Start-Up

To provide an opportunity to assess the suitability and/or potential of using SaniFoam plastic foam ("SaniBlanket") as an intermediate cover material during landfilling of solid wastes, two simulated landfill cells with the necessary appurtenances to permit leachate and gas collection for the single-pass cell as well as leachate recycle for the recycle cell were constructed as shown in Figures 5 and 6. The single-pass cell was intended to simulate conventional landfill practice; the recycle cell, to simulate conditions where leachate is contained, collected and recycled, using the landfill as an *in situ* leachate treatment system.

To initiate the simulated landfill studies, a layer of shredded municipal solid waste was added to both cells, manually compacted, and covered with a 5-cm layer of SaniFoam plastic foam which was allowed to cure overnight. This foam layer was then broken into small fragments and a second layer of compacted solid waste was added to each cell. Characterization of the solid waste placed in the cells is presented in Table 5. (Additional characterization of the solid waste will be conducted as necessary during subsequent phases of the study.)

In order to bring the cells to apparent field capacity and expedite the generation of leachate, 35 liters of distilled water were added to each cell. To minimize short-circuiting, the water was added in small increments and distributed evenly across the surface of the solid waste over a 2-day period. Following this initial addition of water, the cells were sealed to prevent the entry of air and to allow for the collection of gases generated within each of the cells.

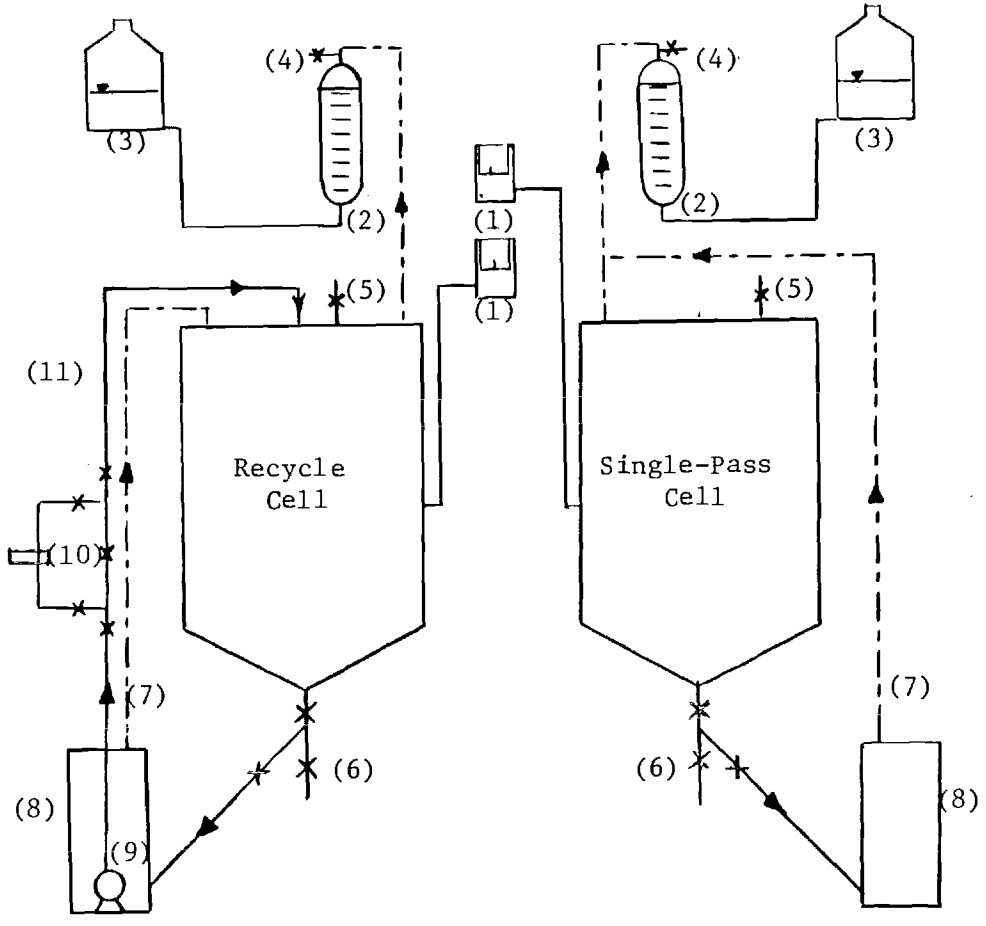

Figure 5. Schematic Diagram of the Simulated Landfill Cells.

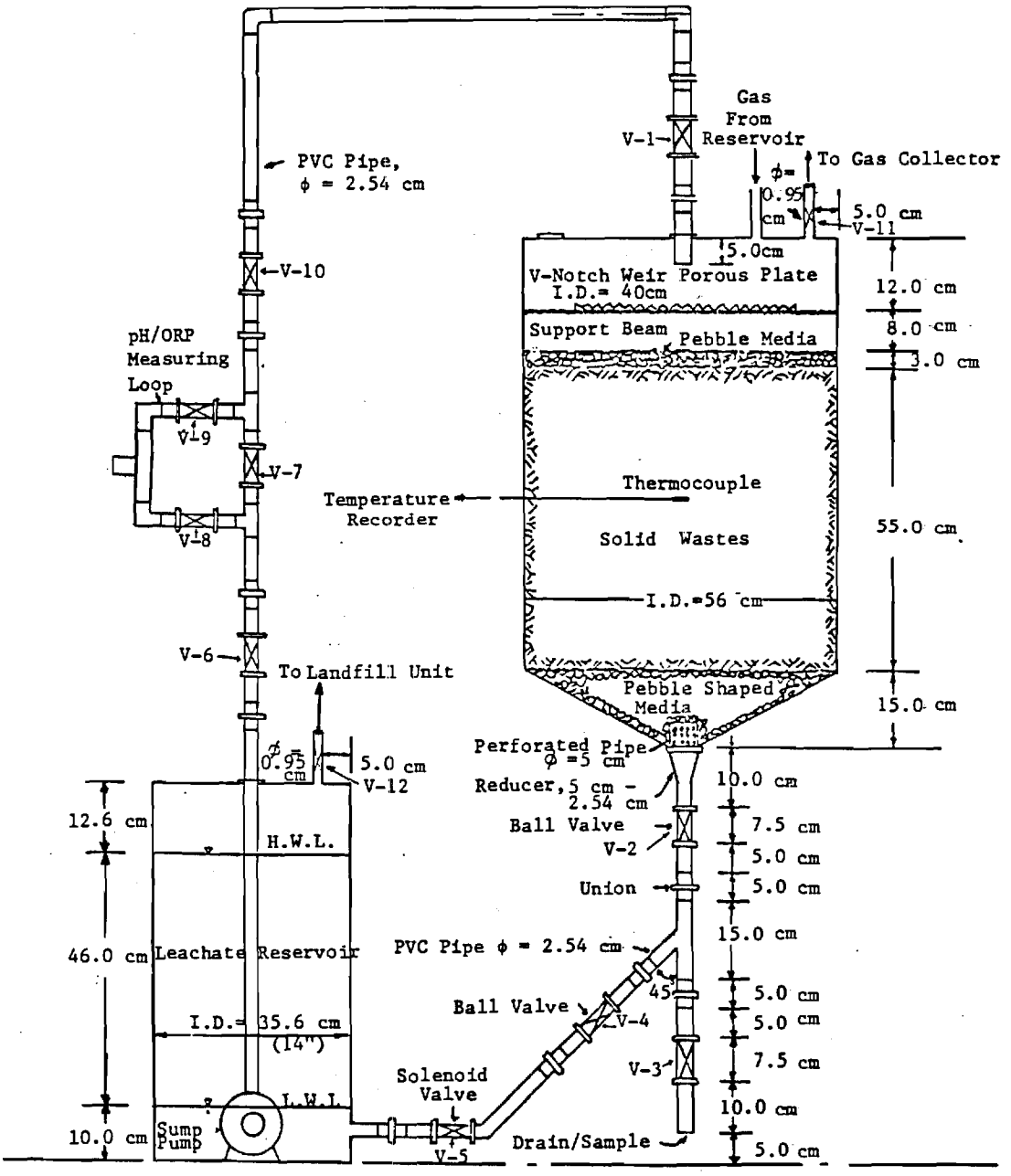

Figure 6. Detailed Drawing of Landfill Cell with Leachate Recycle.

TABLE 5. CHARACTERIZATION OF SOLID WASTE ADDED TO SIMULATED LANDFILL CELLS

Parameter	Single-Pass	Recycle
Amount of solid waste added:		
- as placed	60 kg (132.3 lb.)	60 kg (132.3 lb.)
- dry weight	39 kg (86.0 lb.)	39 kg (86.0 lb.)
Moisture Content	35%	35%
Density	373.5 kg/m (629.6 lb/yd)	372.3 kg/m (627.5 lb/yd)
Volatile Solids	73.4%	74.2%
Amount of foam in cell (% of total solid waste volume)	8%	8%
Carbon (dry weight)	43.8%	43.8%
Hydrogen (dry weight)	5.8%	5.8%
Nitrogen (dry weight)	6.2%	6.2%

Operational Procedures

After the cells were brought to apparent field capacity, additional moisture (distilled water) was added in amounts and at intervals corresponding to rainfall events in the Atlanta area. Information on rainfall is obtained from the meterological station located on the Georgia Tech campus, and data on moisture accumulations for both cells are presented in Figure 7. Moisture addition to the recycle cell was terminated on Day 62 as a sufficient volume of water had been accumulated in this cell to allow for leachate recycle, initiation of landfill stabilization and periodic sample collection for analysis.

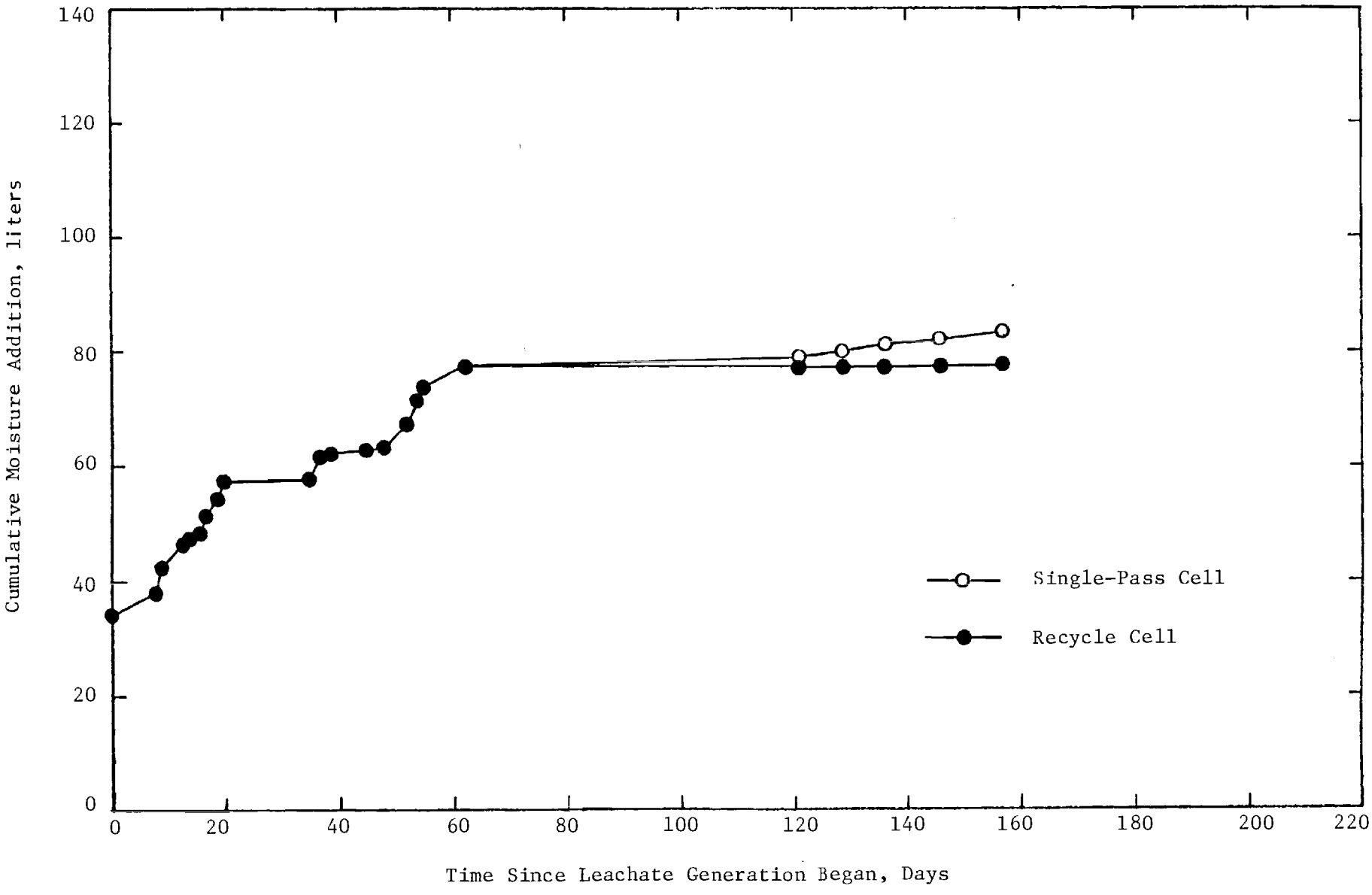

Figure 7. Cumulative Moisture Addition to Simulated Landfill Cells.

Accumulated leachate has been collected and recycled daily in the recycle cell and collected and removed to storage in the single-pass cell. In addition, the volume of gas generated and temperatures are recorded on a daily basis for both landfill systems.

Sample Collection and Analyses

Collection of leachate samples for analyses was initiated when sufficient quantities of leachate were generated by the cells and has continued at periodic intervals (approximately weekly). Samples of gases produced by the cells are also collected and analyzed at periodic intervals. These analyses will be used to determine the stage of landfill decomposition. Analyses being performed on the leachate samples include: pH, Oxidation-Reduction Potential (ORP), conductivity, total alkalinity, volatile acids, COD, BOD_5, TOC, chlorides, sulfides, selected metals and formaldehyde. Gas samples are analyzed for relative composition of nitrogen, carbon dioxide, oxygen, hydrogen and methane.

Presentation and Discussion of Results

Landfill Cell Temperature. Landfill cell temperatures varied with the ambient temperature of the room where the cells are located as indicated in Figure 8. There has been a gradual decreasing temperature trend corresponding to seasonal changes. The temperatures within both cells have been very similar with differences being less than 1°C on most occasions. Hence, the effect of temperature differences on biological activity within the cells was considered minimal.

Leachate Characterization. Results from the analyses of leachate samples indicate that acid fermentation has begun in both cells as evidenced by the high concentrations of BOD_5, TOC, COD and volatile acids (Figures 9-14). The initial high concentrations of BOD_5, TOC, and COD are a result

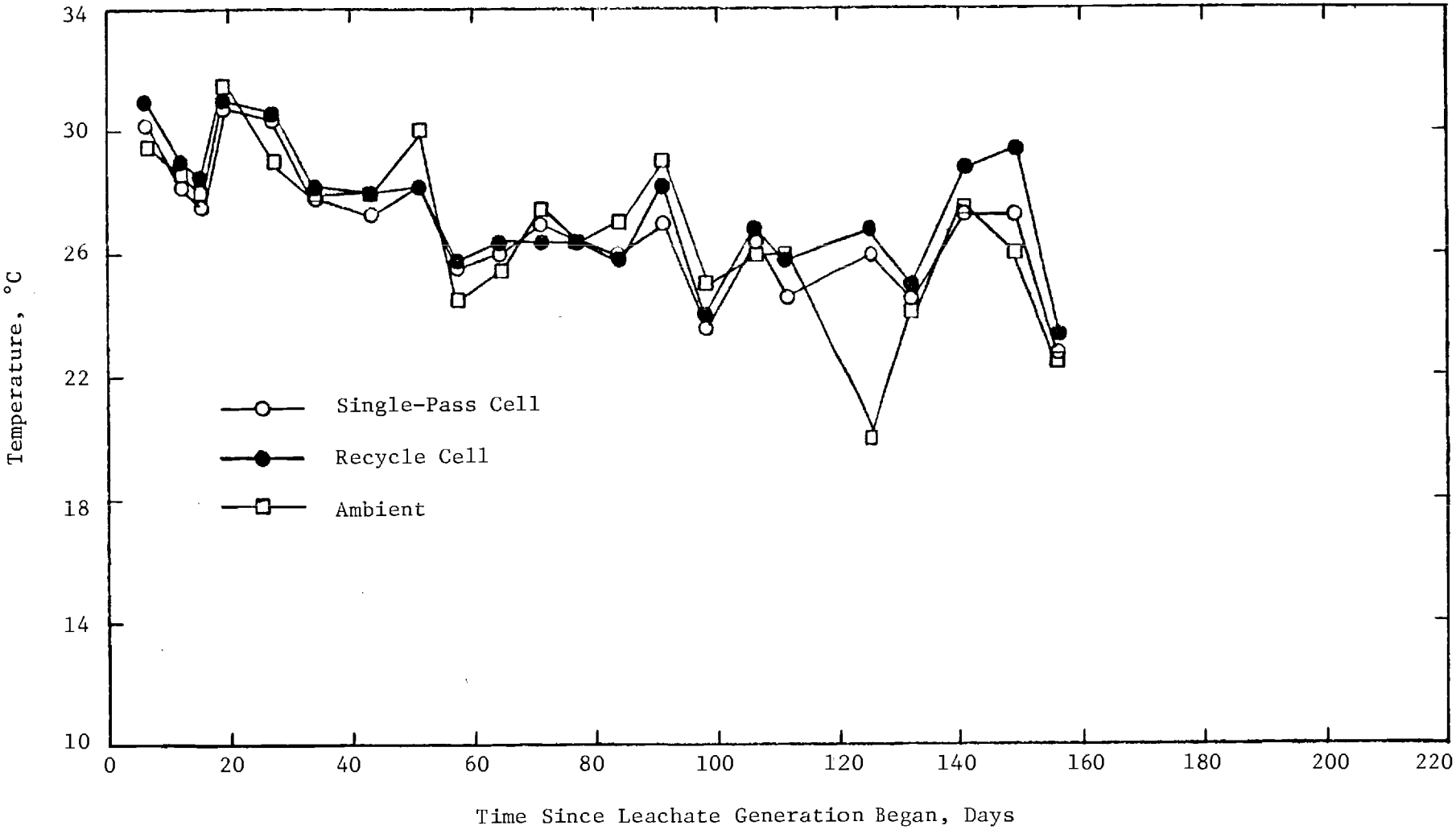

Figure 8. Ambient and Simulated Landfill Cell Temperatures

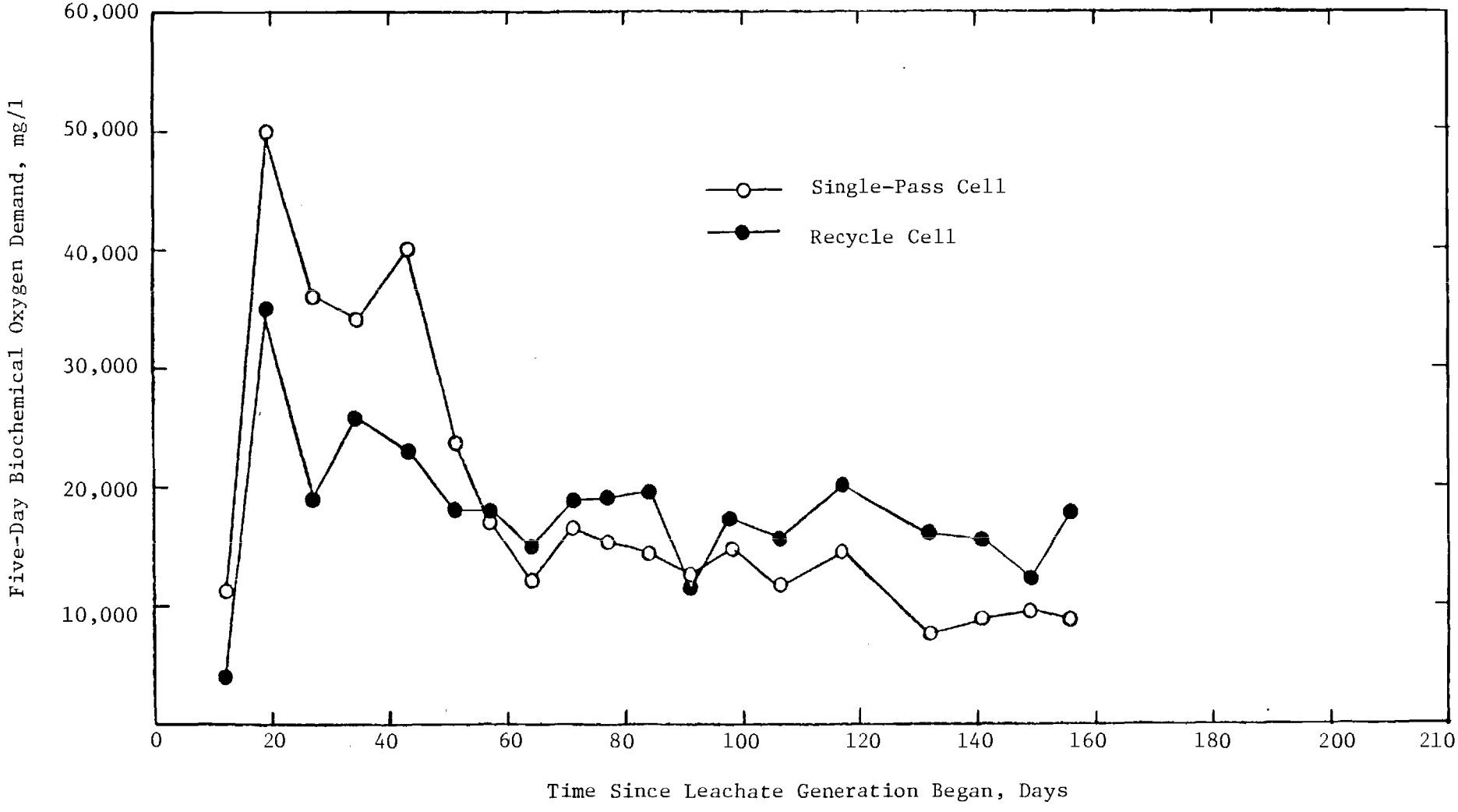

Figure 9. Five-Day Biochemical Oxygen Demand of Leachate.

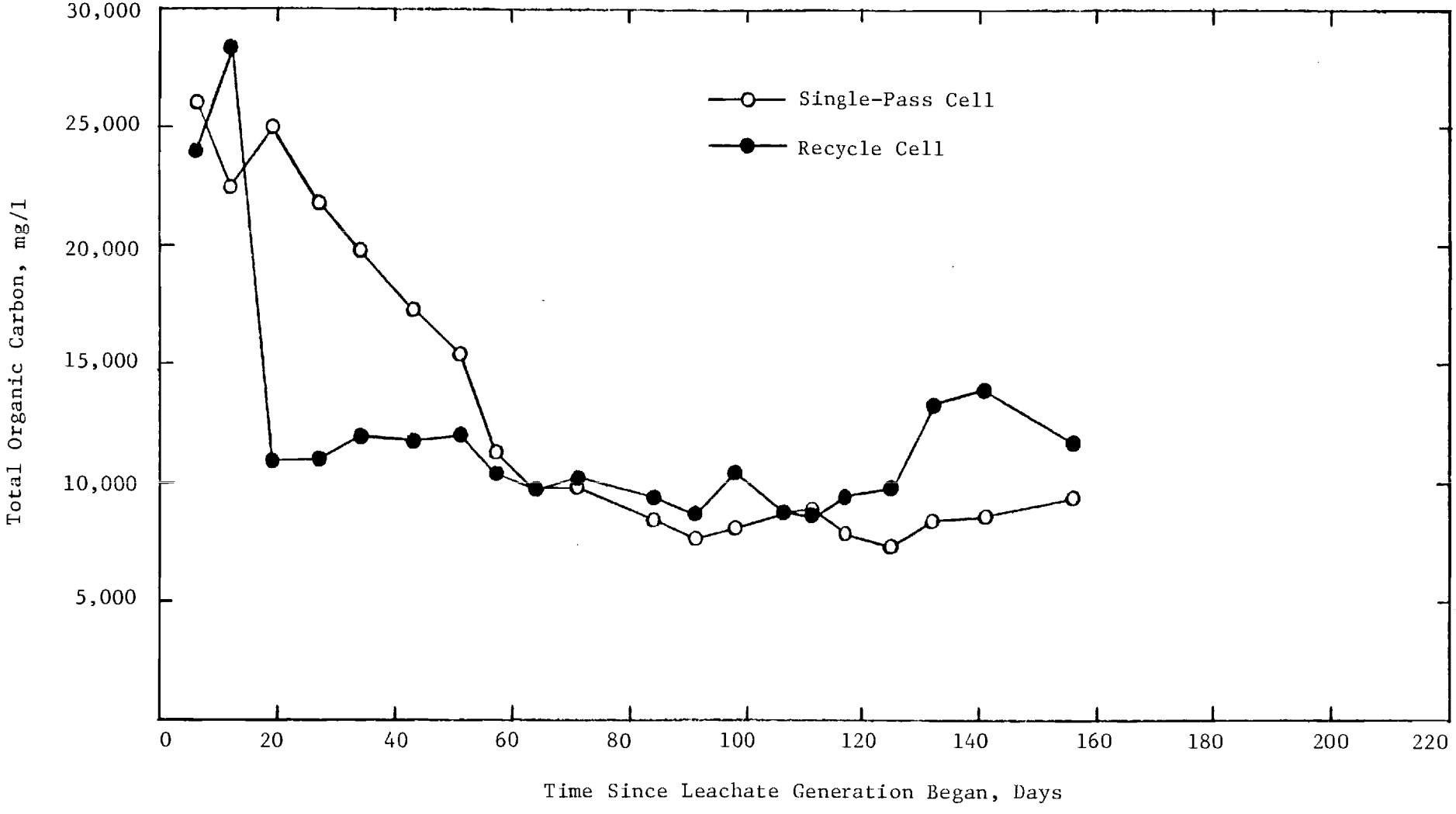

Figure 10. Total Organic Carbon Content of Leachate.

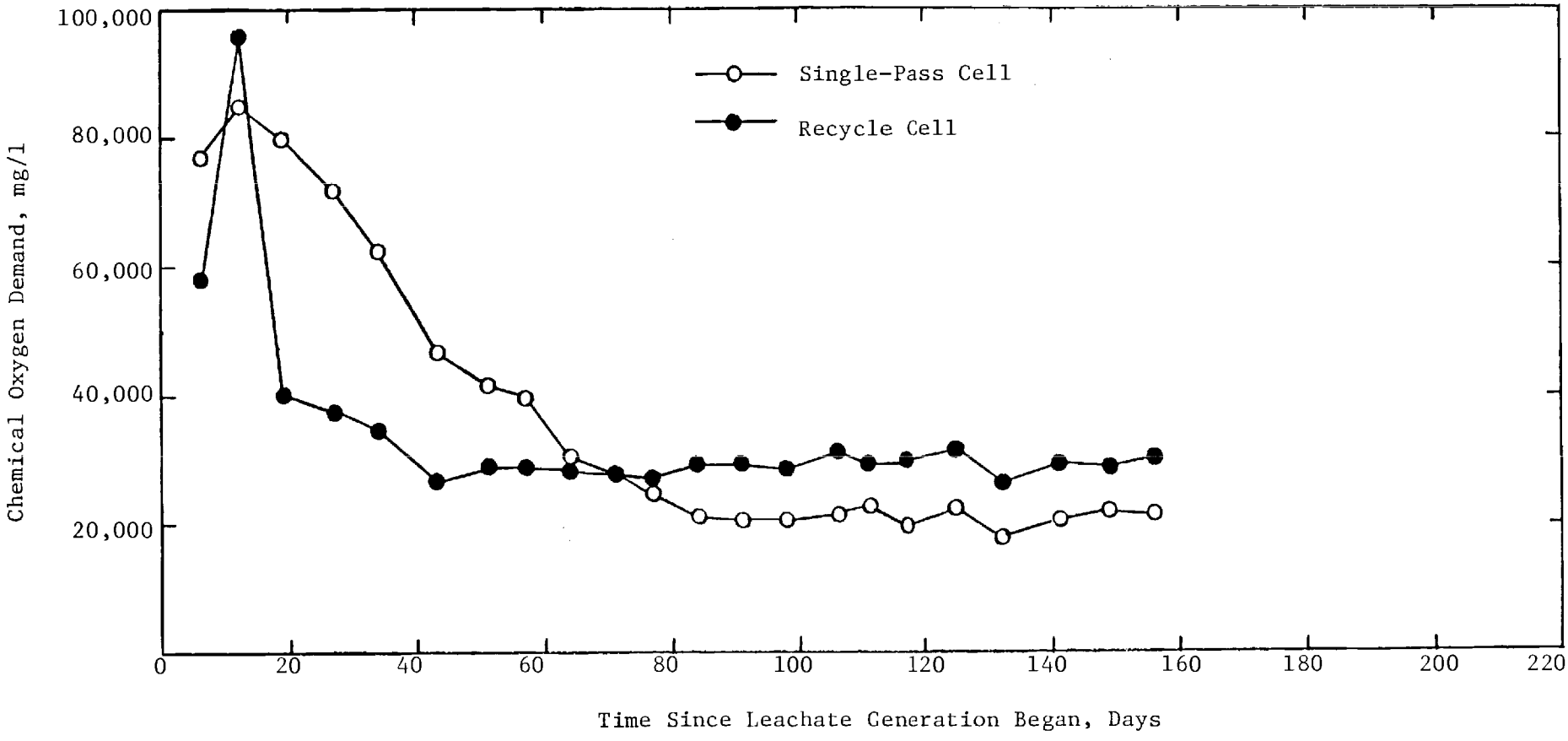

Figure 11. Chemical Oxygen Demand of Leachate.

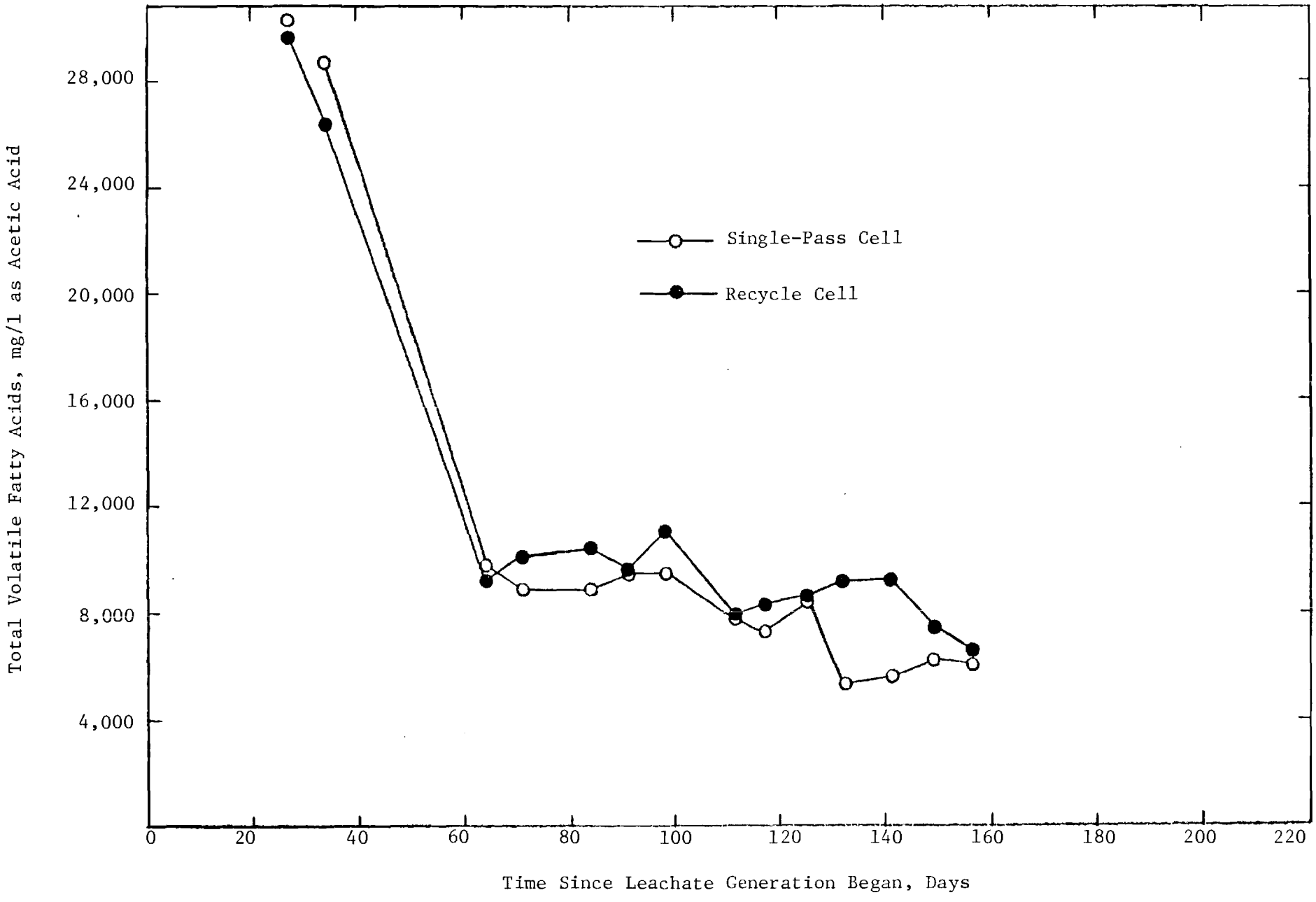

Figure 12. Total Volatile Fatty Acids Content of Leachate.

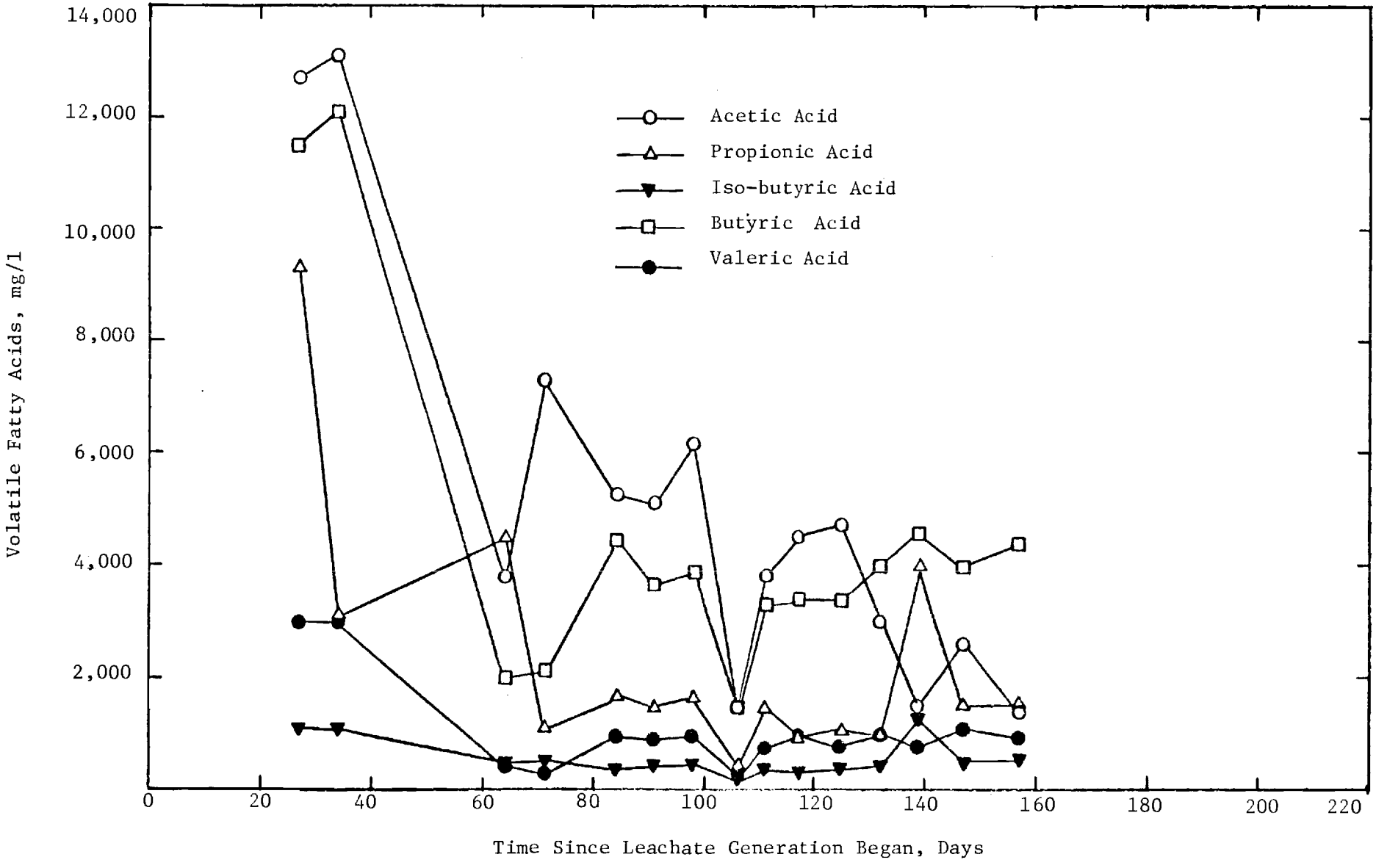

Figure 13. Individual Volatile Fatty Acids Content of Leachate from the Recycle Cell

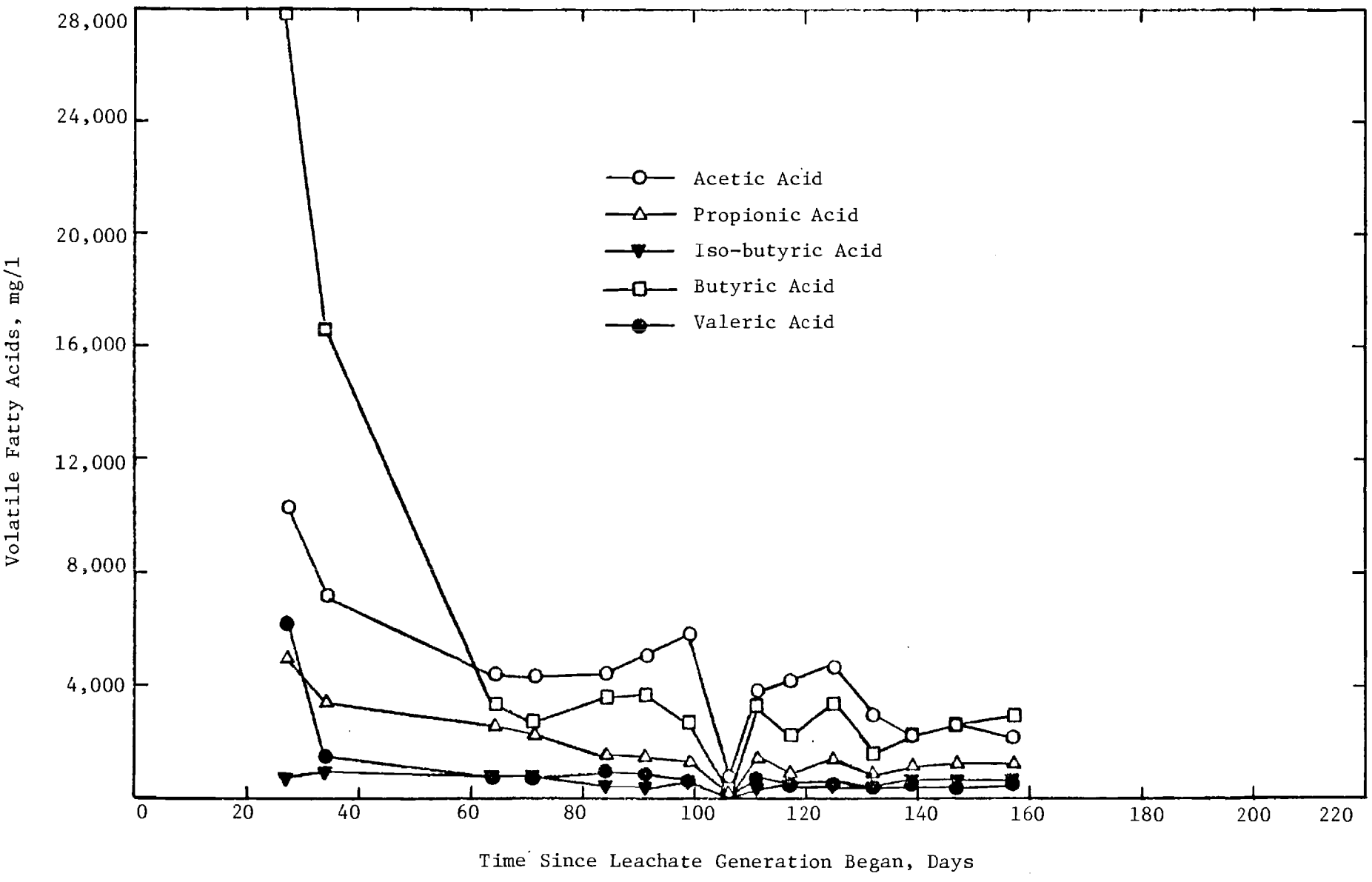

Figure 14. Individual Volatile Fatty Acids of Leachate from the Single-Pass Cell.

of the solubilization of organics present in the solid waste as well as conversion of complex organics to simpler compounds. The high concentration of volatile acids is attributed to the conversion of readily biodegradable organics to short-chain fatty acid intermediates by acid producing bacteria. The decrease in the concentration of BOD_5, TOC, COD and volatile acids that occurred between Days 35 and 65 was attributable to the dilution effect of moisture addition during this time period (see Figure 7) in the recycle cell and the washout and removal of these constituents from the single-pass cell.

The higher concentrations of these parameters in the leachate from the recycle cell as compared with the single-pass cell is attributable to the different removal mechanisms in each cell. In the recycle cell, daily recycle of leachate provided a continuing exposure of the microbial populations present to nutrients contained in the leachate, thereby enhancing overall conversion of these constituents to end-products (CO_2 and CH_4). Because the leachate is contained within the cell, this mechanism initially results in higher concentrations of pollutants than in the single-pass cell where the organics present within the solid waste are washed out by single-pass moisture addition and are, therefore, less available for the microbial utilization. As a result, lower concentrations of organic pollutants were measured in the single-pass cell, a lower overall percentage of organic pollutant treatment could be expected, and the potential of pollution from the leachate would be more prevalent if the leachate was released to the environment.

The initial decrease of the pH during Days 15 to 35 and subsequent low pH values (Figure 15) were attributable to the corresponding increase in volatile acids during this period. Similarly, high conductivity of the leachate from both cells (Figure 16) was due to the formation of volatile

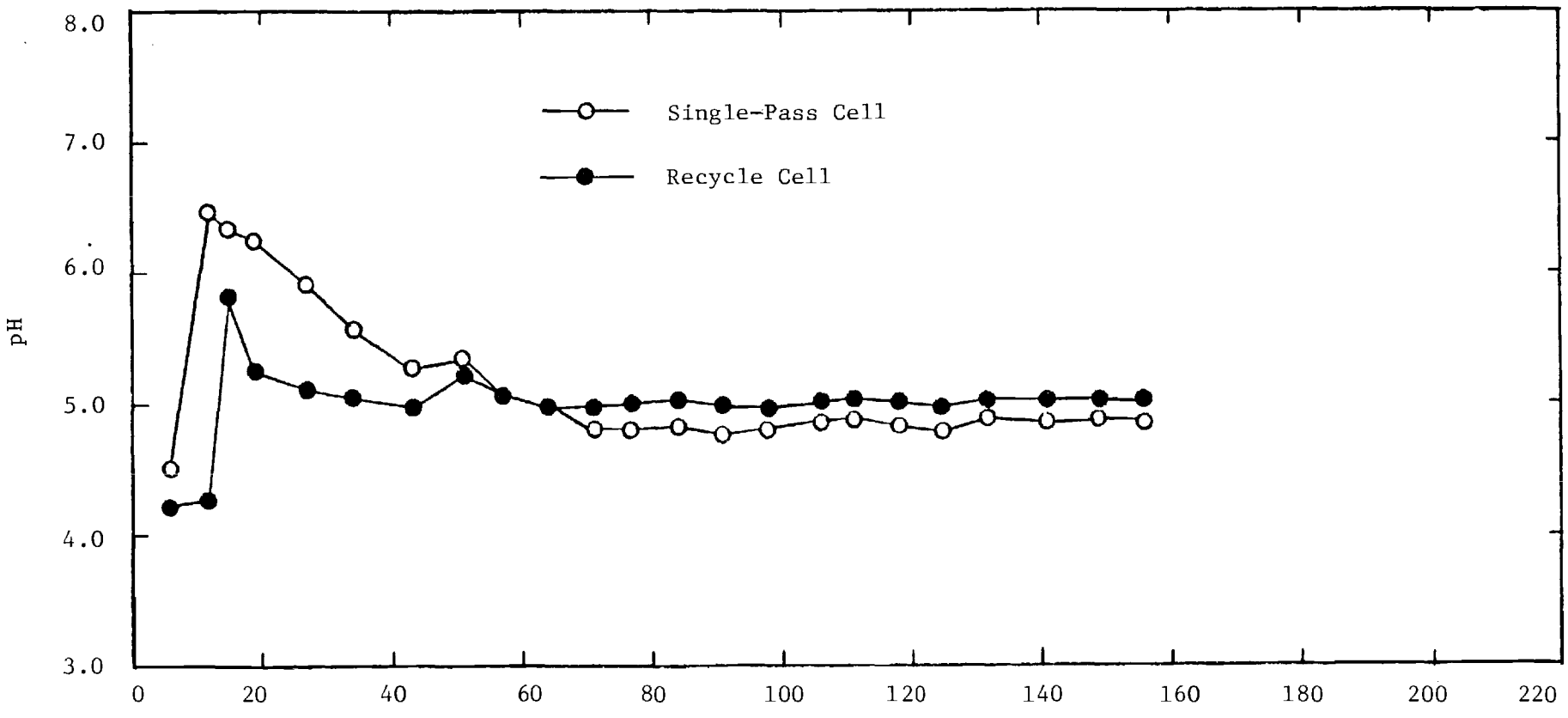

Figure 15. pH of Leachate

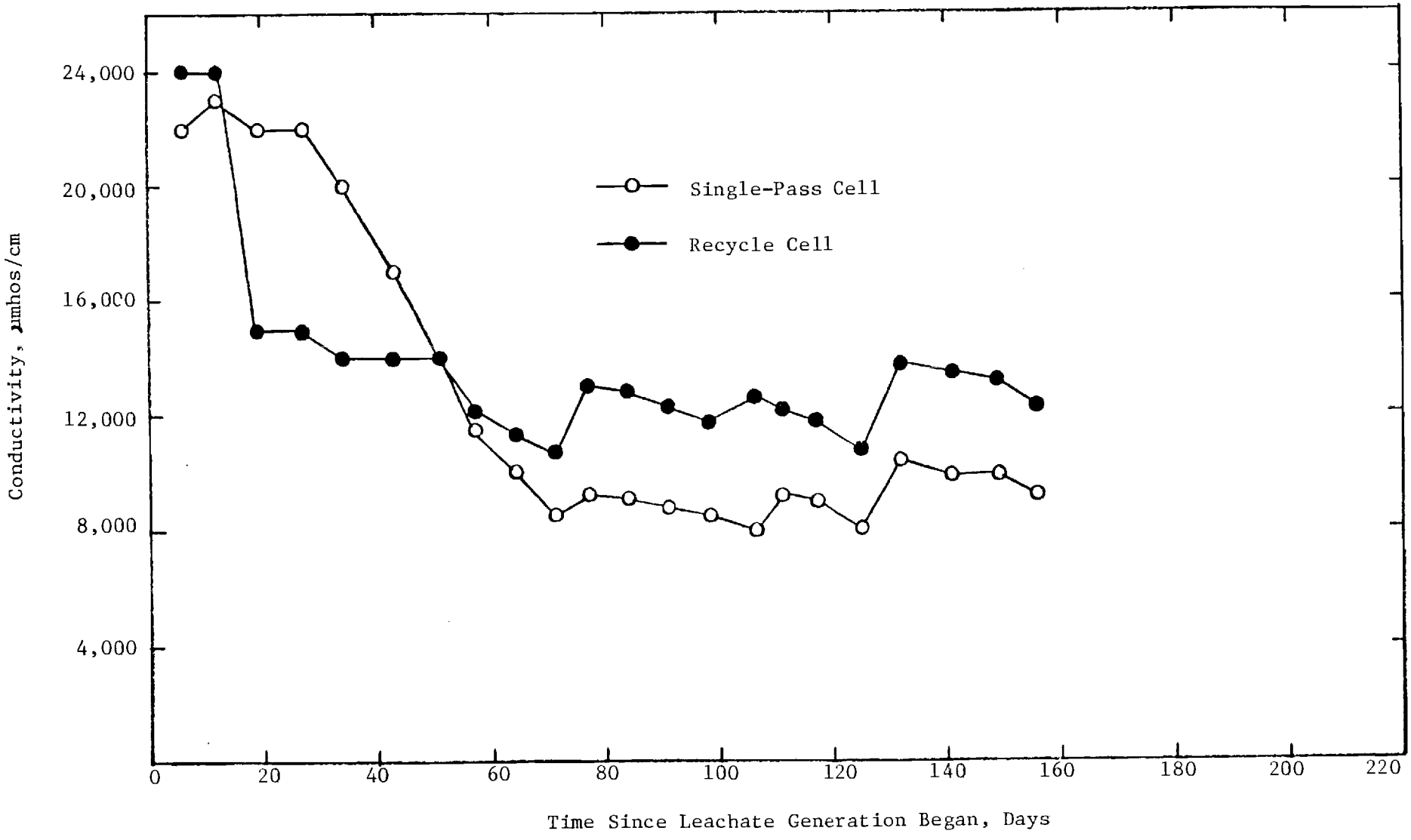

Figure 16. Conductivity of Leachate.

acids and the release of organic and inorganic constituents by the physical and biochemical processes occurring during the early stages of landfill stabilization. The subsequent decrease in conductivity between Days 12 and 60 was attributable to the dilution and washout effect in the recycle and single-pass cells, respectively, as discussed previously.

The alkalinity of the leachate samples is an indicator of the buffer capacity of the system. The initial increase in alkalinity in the leachate of both cells (Figure 17) was attributed to the corresponding increase in volatile acids during this period. The decrease observed between Days 12 and 55 again reflected the effects of dilution and washout.

The results of the Oxidation-Reduction Potential (ORP) measurements on the leachate from both cells are presented in Figure 18. Negative ORP values indicate that both cells are presently operating under reduced conditions, which are conducive to anaerobiosis. However, these values were apparently not low enough to permit the complete transformation of sulfates and sulfites to sulfides as highly reduced conditions (ORP values of less than -200 mV E_c) are necessary for this to occur. To date, sulfides have not been detected in the leachates from either cell.

Analysis of chlorides was performed to enable estimation of the dilution effects resulting from moisture addition to the cells. The chloride ion was selected because of its high solubility and ion reactivity with other constituents in the leachate. The chlorides concentration of the leachate samples (Figure 19) varied inversely with the total volume of moisture added to the cells (Figure 3).

Leachate samples were also analyzed for selected heavy metals that were expected to be present in the solid waste and/or that could have potentially adverse environmental or health impacts. These included mercury (Hg),

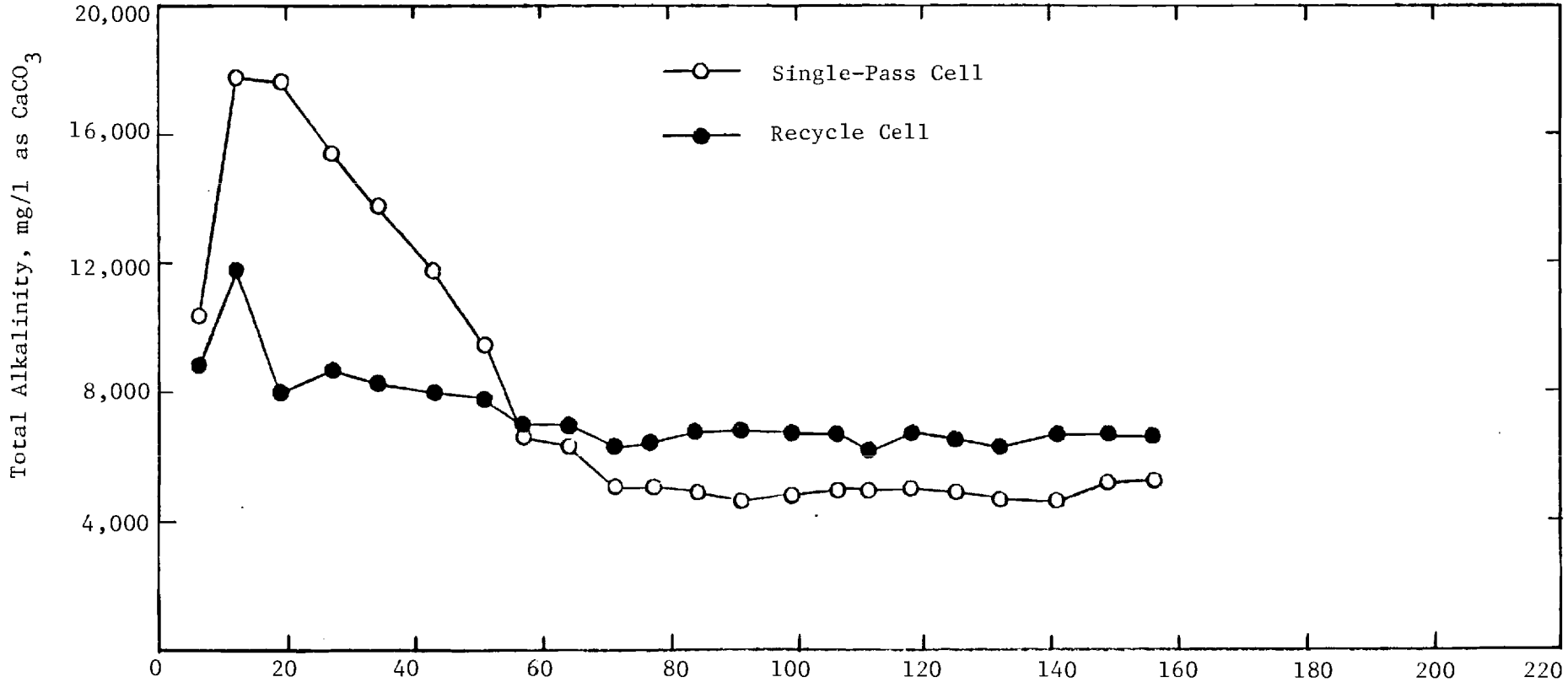

Figure 17. Total Alkalinity of Leachate.

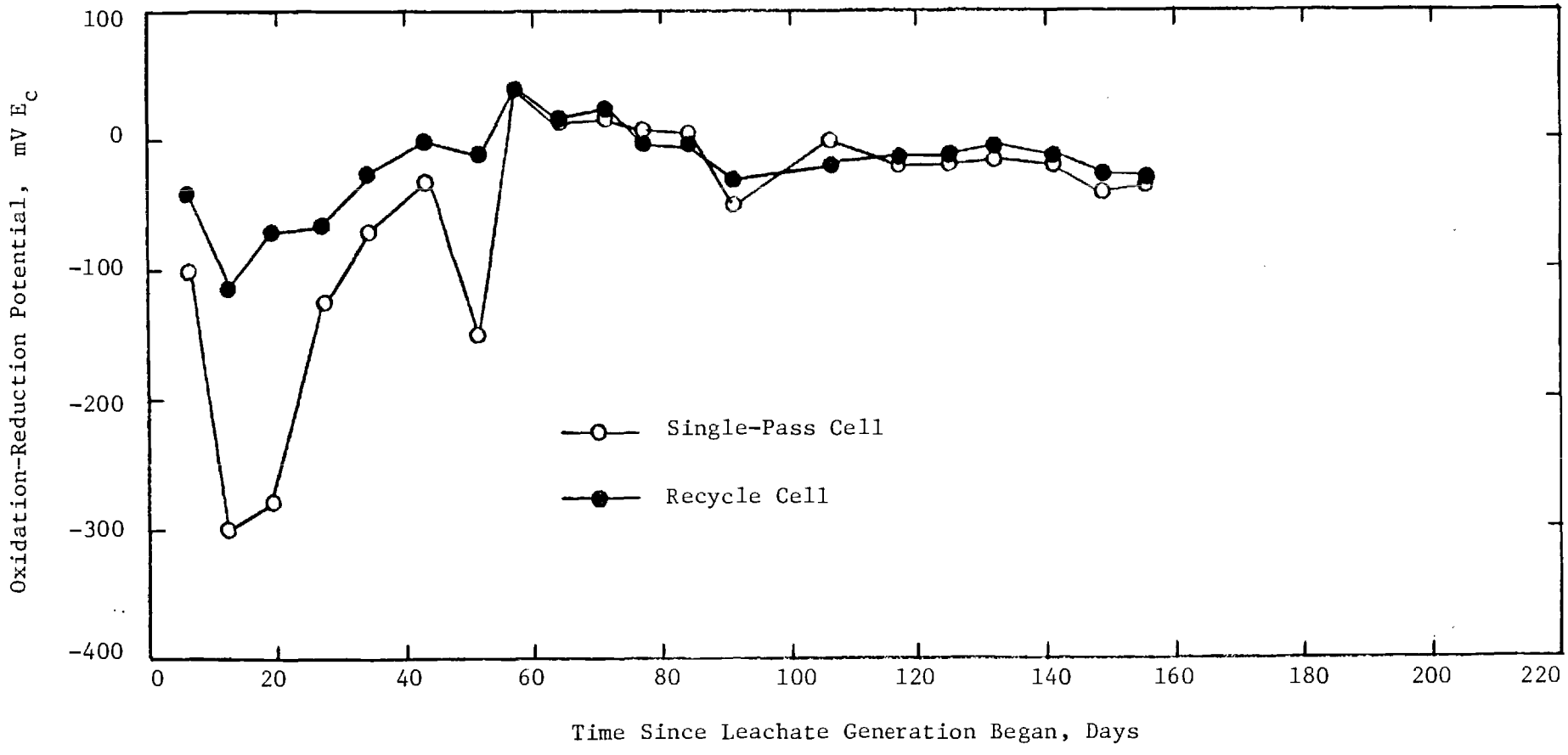

Figure 18. Oxidation - Reduction Potential of Leachate.

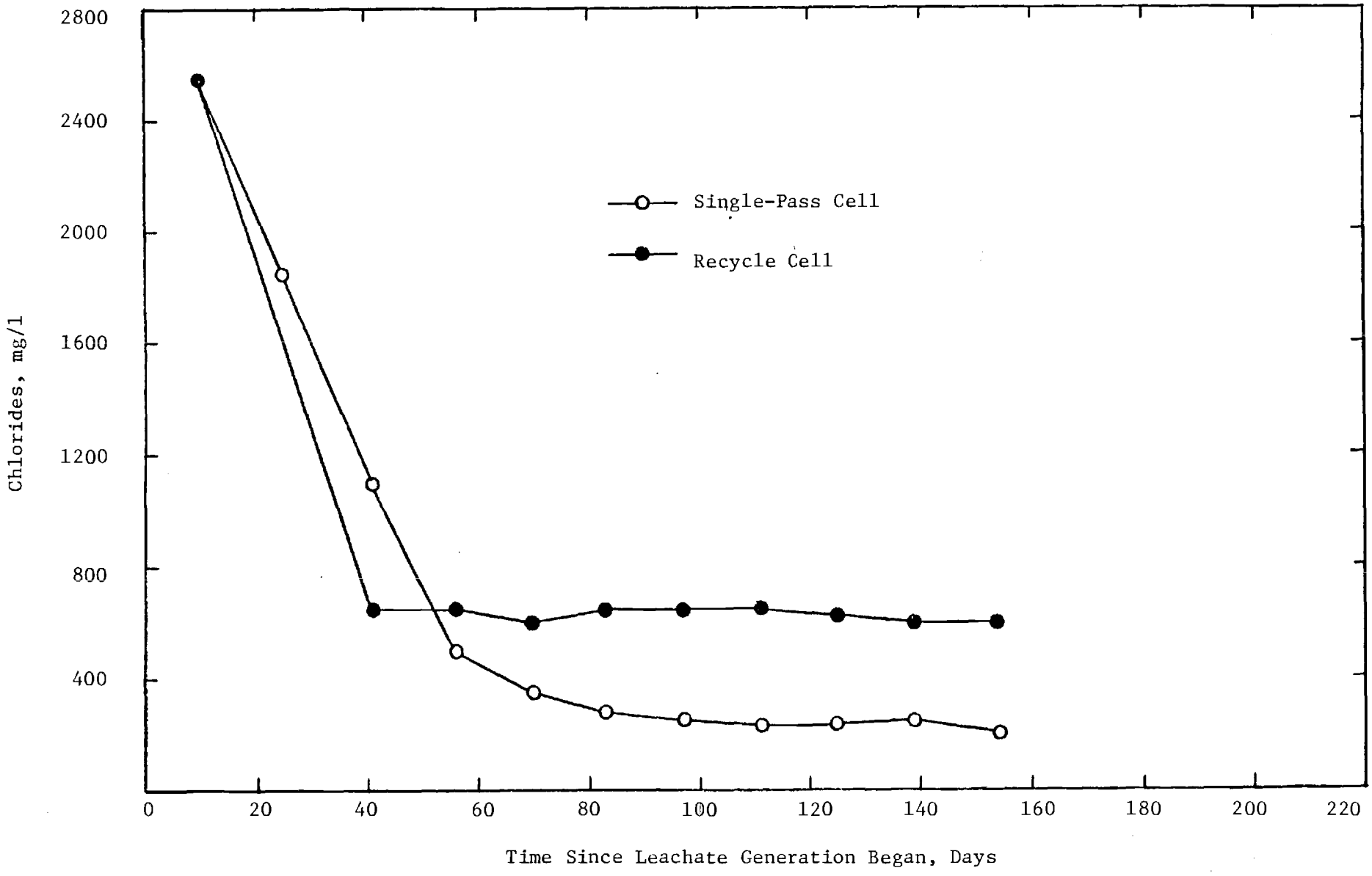

Figure 19. Concentration of Chlorides in Leachate.

cadmium (Cd), chromium (Cr), iron (Fe) and zinc (Zn). The results of analyses to date are presented in Table 6 and indicate that mercury and cadmium were not detected in the leachate, and low concentrations of chromium were detected only in the initial samples. The concentrations of iron and zinc were considered representative of a landfill in the early stages of decomposition as the acid conditions within the landfill resulted in the solubilization of these metals. Presence of sulfides as conditions become more reducing will likely lead to their precipitation as insoluble metal sulfides.

Gas Production. Cumulative gas production for both cells is presented in Figure 20. The lack of any significant gas production to date by both systems indicated that acid fermentation was predominant in both cells and that conversion of acids to CH_2 and CO_2 had not yet been achieved.

Formaldehyde Concentrations. Initial attempts to detect and quantify formaldehyde in the leachate were made using direct injection, packed column GC; direct aqueous injection, capillary column GC-MS; and, the chromatropic acid colorimetric methods. The results of these analyses are summarized in Table 7. The direct aqueous injection, packed column GC method produced poor separation of the formaldehyde peak from other peaks in both the samples and standards. This prevented reliable determination of formaldehyde concentrations, and this method was, therefore, abandoned.

Formaldehyde was not detected in either leachate sample by direct aqueous injection capillary column GC-MS. This determination was made by comparison of chromatograms of a formaldehyde standard solution with those of the leachate samples and the leachate samples spiked with formaldehyde (Figures 21 through 25, respectively). Although the direct aqueous injection, GC-MS method was able to positively identify formaldehyde, the

TABLE 6. CONCENTRATIONS OF METALS IN LEACHATE SAMPLES

Sample Date	Day	Hg, mg/l** Single-Pass	Hg, mg/l** Recycle	Cd, mg/l Single-Pass	Cd, mg/l Recycle	Cr, mg/l Single-Pass	Cr, mg/l Recycle	Fe, mg/l Single-Pass	Fe, mg/l Recycle	Zn, mg/l Single-Pass	Zn, mg/l Recycle
7/23/82	12	N.D.	N.D.	N.D	N.D.	1.5	1.5	--	--	200	162
8/07/82	27	--	N.D.	N.D.	N.D.	0.8	N.D.	400	600	178	50
8/23/82	43	N.D.	N.D.	N.D.	N.D.	0.8	N.D.	700	600	175	43
9/07/82	58	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	430	520	125	40
9/21/82	71	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	400	500	110	39
10/05/82	85	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	480	600	50	43
10/18/82	98	--	--	--	--	--	--	400	600	45	25
11/01/82	111	--	--	--	--	--	--	650	450	50	25
11/15/82	125	--	--	--	--	--	--	800	630	40	35
11/29/82	141	--	--	--	--	--	--	850	300	28	16
12/14/82	156	--	--	--	--	--	--	950	750	30	37

*Detection Limits: Mercury (Hg) - 50 mg/l
Cadmium (Cd) - 0.5 mg/l
Chromium (Cr)- 0.5 mg/l
Iron (Fe) - 0.5 mg/l
Zinc (Zn) - 0.5 mg/l
N.D. = Not detected.

**Because of the high detection limit of mercury by this method, selected samples will also be analyzed by the cold vapor method which has a lower detection limit.

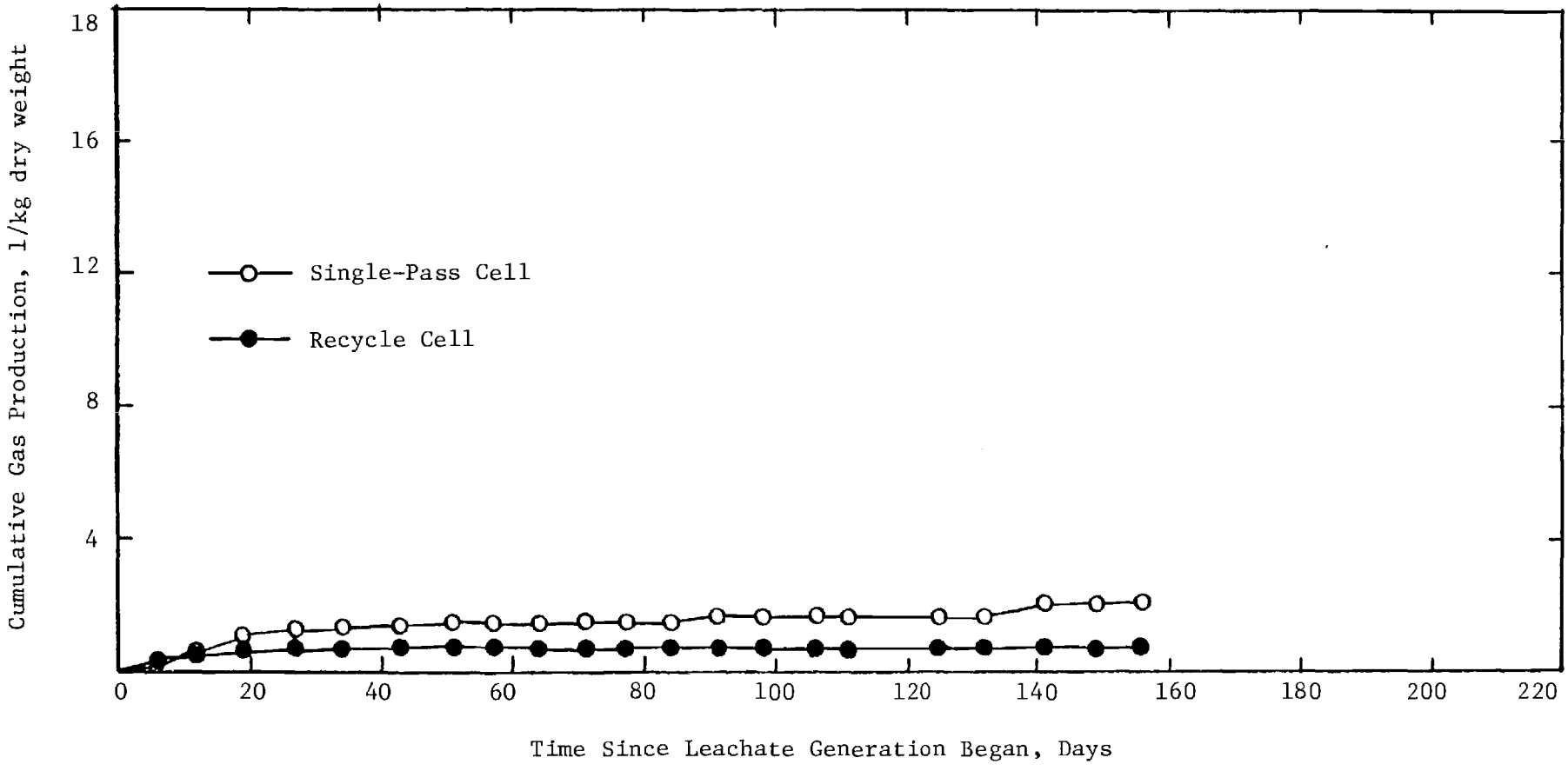

Figure 20. Cumulative Gas Production from the Simulated Landfill Cells.

TABLE 7. RESULTS OF THE DETERMINATION OF FORMALDEHYDE IN LEACHATE FROM THE SINGLE-PASS LANDFILL CELL BY GAS CHROMATOGRAPHY, GAS CHROMATOGRAPHY-MASS SPECTROSCOPY, AND THE CHROMATROPIC ACID METHODS

Analytical Method*	Sampling Date 8/7/82	9/29/82	Comments
Direct Aqueous Injection, Gas Chromatrographic Technique	--	--	Poor separation of the formaldehyde peak from other peaks in both samples and standards prevented reliable determination of formaldehyde directly from aqueous solutions.
Direct Aqueous Injection, Capillary Column Gas Chromatography-Mass Spectroscopy (GC-MS) Technique	N.D.**	N.D.**	Formaldehyde can be specifically identified with a detection limit of 100 mg/1. Therefore, formaldehyde was not present in the leachate in concentrations greater than 100 mg/1.
Chromatropic Acid, Colorimetric Method	270 mg/1	30 mg/1	A positive reaction with the reagent occurred and, if the color development was solely attributable to formaldehyde, significant concentrations of formaldehyde could be present in the leachate samples. Reliability decreases with complexity of mixture (e.g., leachate) due to interferences with positive reaction with the reagent. (Since the GC-MS method is not subject to such interferences and did not detect formaldehyde in concentrations above 100 mg/1, color development was at least partially attributable to the reaction of other constituents present in the leachate.) Therefore, the method was not reliable for the determination of formaldehyde in the complex leachate samples.

*See Appendix A for a more detailed description of these analytical methods.
**N.D. - Not detected.

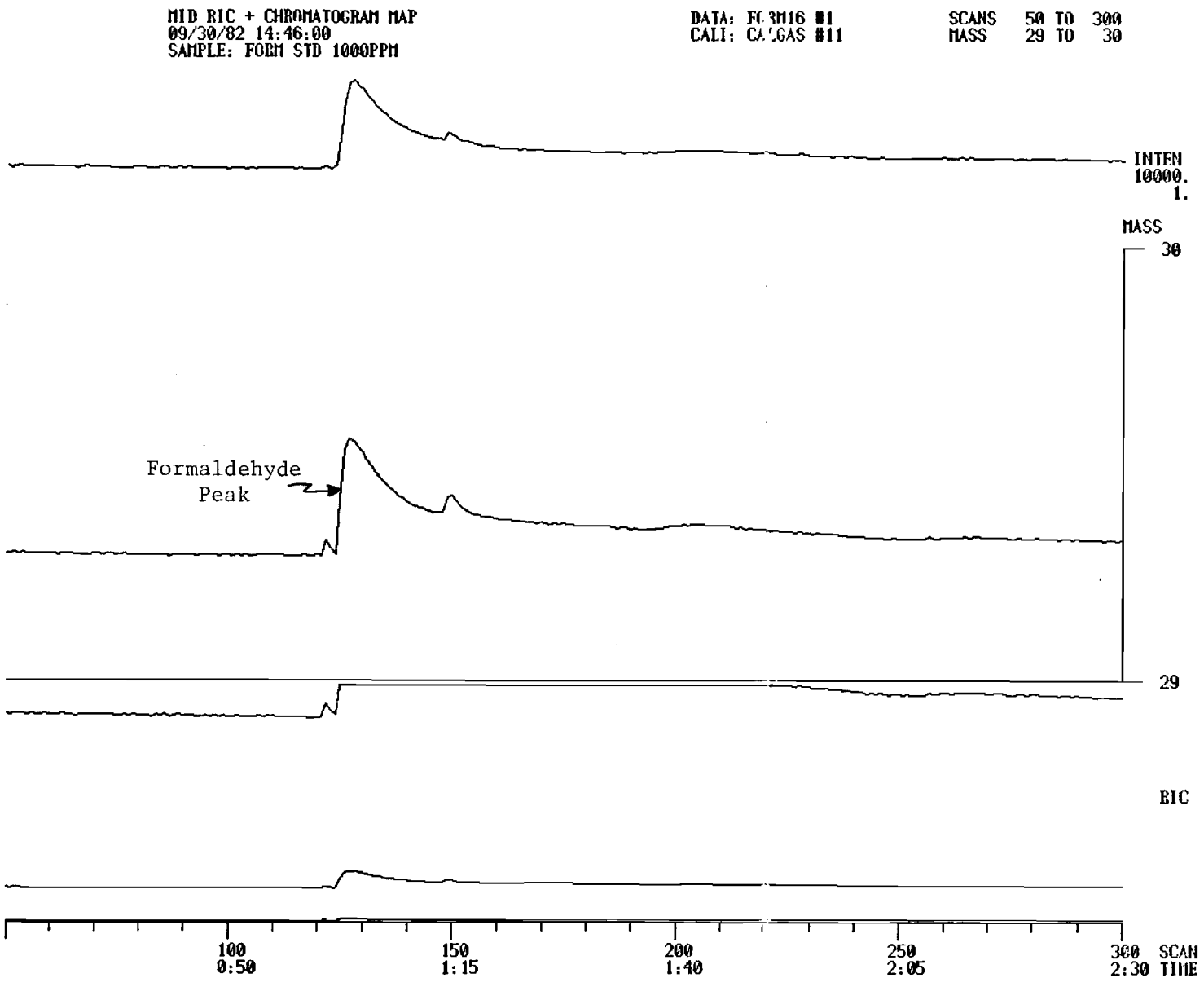

Figure 21. Fragmentogram of Formaldehyde Standard.

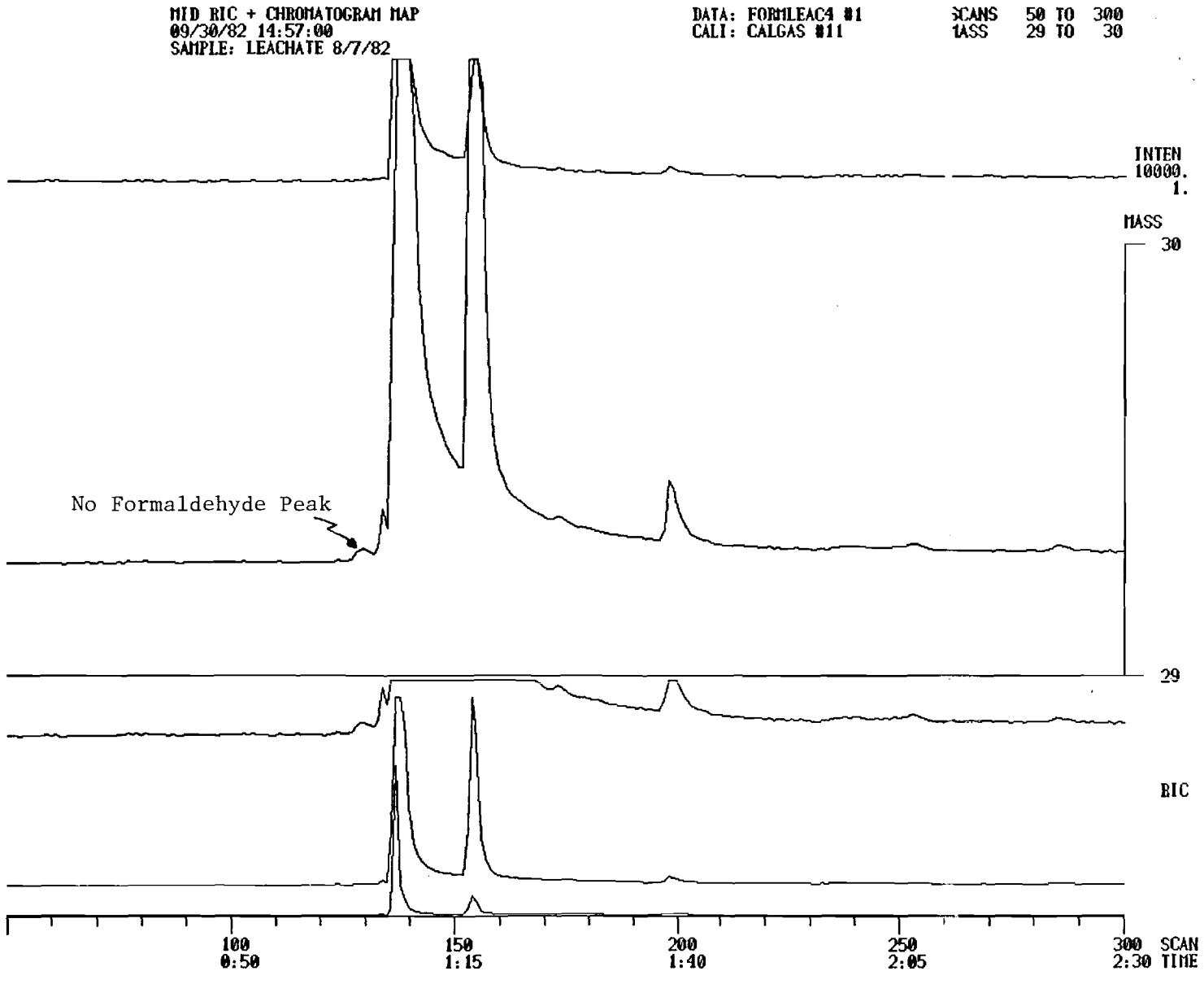

Figure 22. Fragmentogram of Formaldehyde in Leachate from Single-Pass Cell (8/07/82).

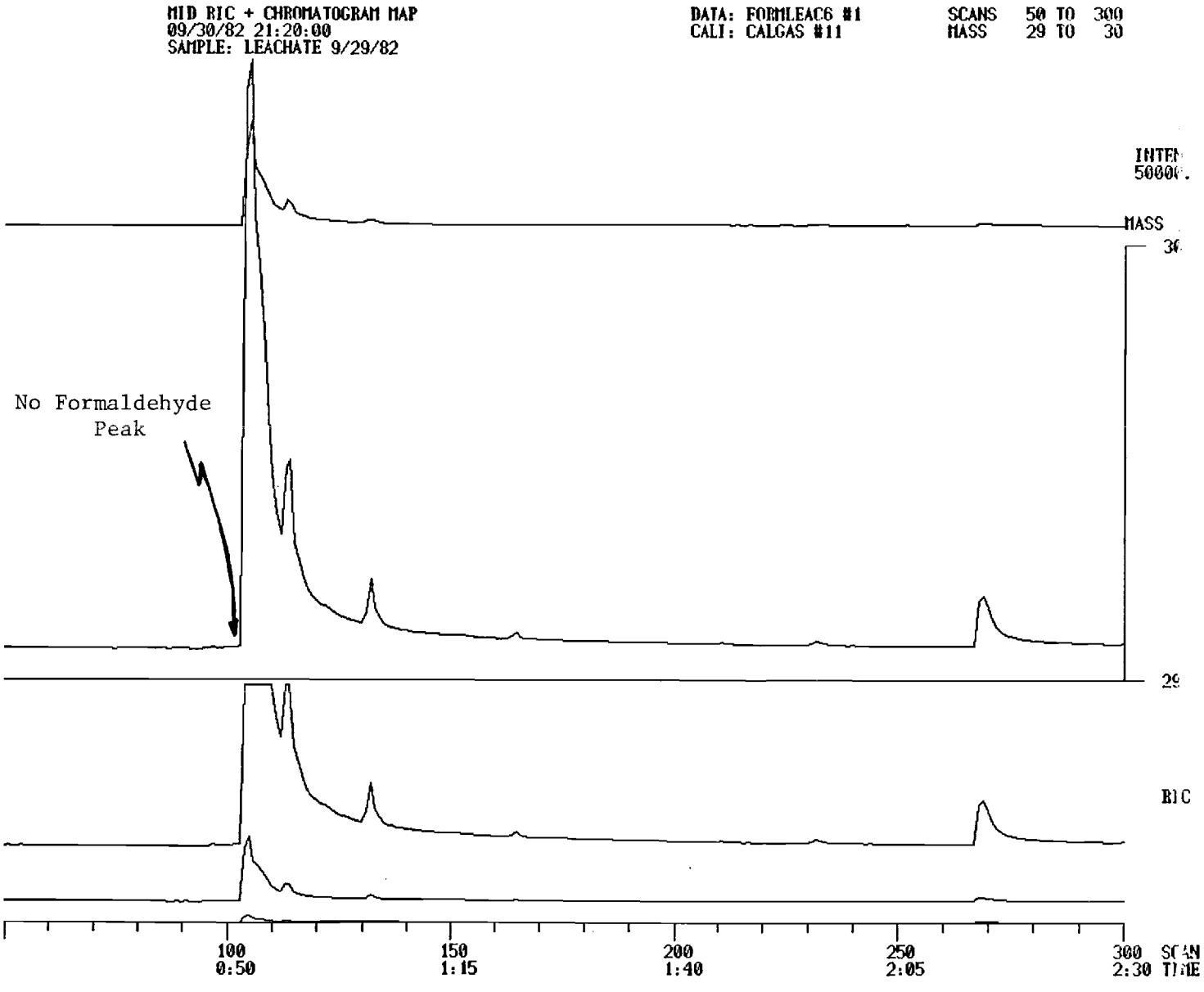

Figure 23. Fragmentogram of Formaldehyde in Leachate of Single-Pass Cell (9/29/82).

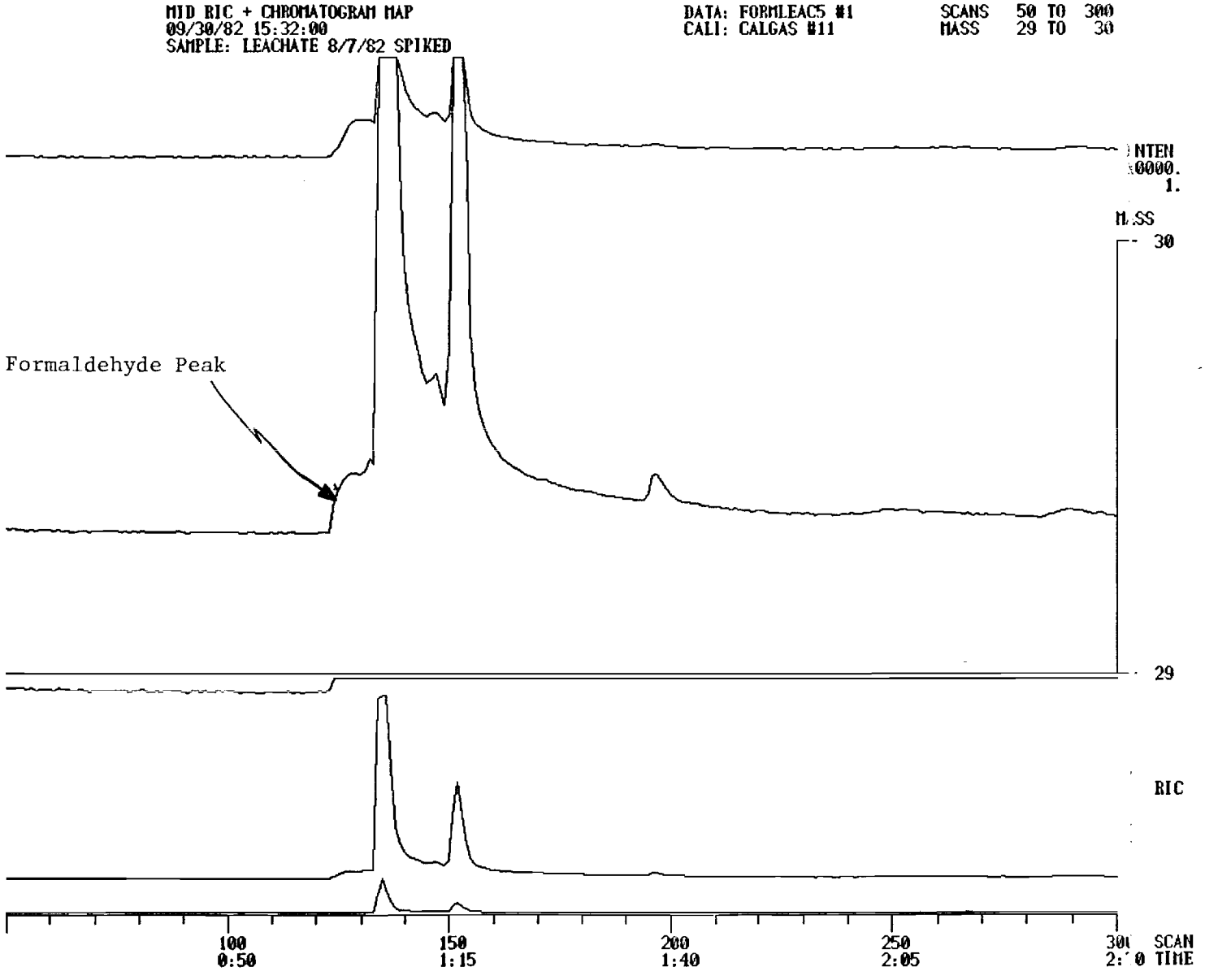

Figure 24. Fragmentogram of Formaldehyde in Spiked Leachate Sample from Single-Pass Cell (8/07/82).

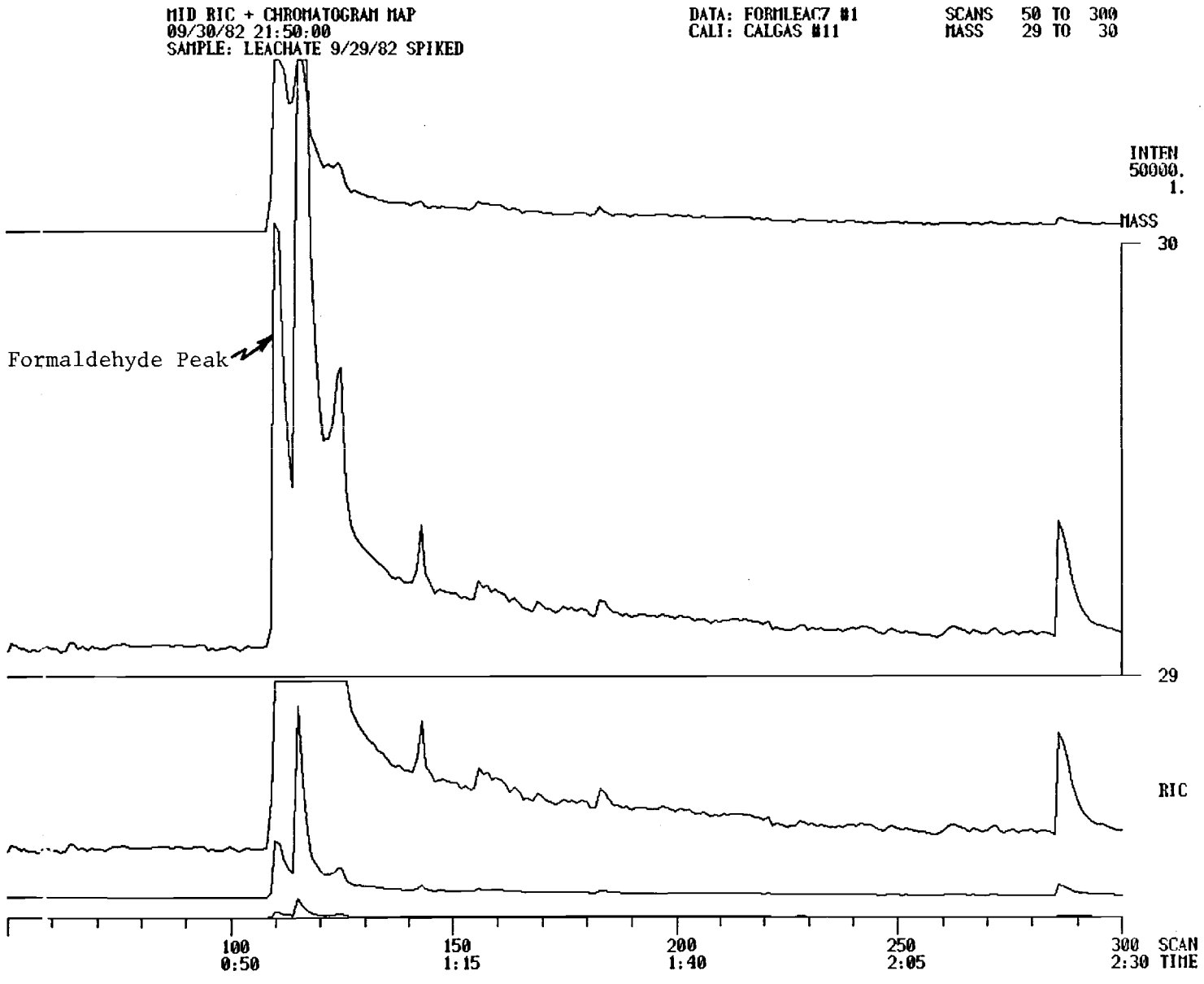

Figure 25. Fragmentogram of Formaldehyde in Spiked Leachate Sample from Single-Pass Cell (9/29/82).

detection limit was $\geqslant$ 100 mg/l. Consequently, this method only indicated that formaldehyde was not present in the leachate in concentrations greater than 100 mg/l.

Analysis of the leachate samples by the chromotropic acid colorimetric method resulted in a positive reaction with the reagent in both samples. The color intensity of the samples, if color development was only due to the reaction of formaldehyde with the chromotropic acid reagent, indicated a formaldehyde concentration of 270 mg/l and 30 mg/l in the leachate samples collected on 8/07/82 and 9/29/82, respectively. However, as previously discussed in Table 2, the reliability of this method decreases when used with complex mixtures due to interferences of other compounds present that can interfere with the formation and/or intensity of color development. Since the GC-MS method, which is most specific with respect to detecting the presence or absence of formaldehyde in concentrations of greater than 100 mg/l, did not detect any formaldehyde in the sampled collected on 8/07/82, it could be concluded that the color development was at least partially attributable to the reaction of the reagent with other constituents present in the leachate. Hence, the method was not reliable for the determination of formaldehyde in the complex leachate samples.

Because of the limitations of each of these analytical methods for the determination of formaldehyde in leachate, no further analyses of leachate samples by these methods has been attempted. Subsequent analyses of leachate samples have been performed by use of the DNPH derivatization method previously discussed. Results of these analyses to date are presented in Table 8 and indicate that low concentrations (3-15 mg/l) of formaldehyde were present in leachate from the single-pass cell. Since these samples were analyzed immediately upon collection from the cell, these concentrations are

TABLE 8. RESULTS OF THE DETERMINATION OF FORMALDEHYDE IN LEACHATE FROM THE SINGLE-PASS LANDFILL CELL

Collection Date of Sample	Formaldehyde Concentration, mg/l	Comments
11/06/82	5.1	Single sample extracted with methylene chloride.
11/11/82	14.3 ± 8.0	Based on 4 samples extracted with methylene chloride.
11/17/82	8.75 ± 4.0	Based on 3 samples extracted with methylene chloride.
11/24/82	3.3 ± 1.7	Based on 3 samples extracted with hexane.

*Determinations were made by derivatization of formaldehyde as 2,4-dinitrophenylhydrazone (DNPH). Concentrations reported assume complete derivatization of formaldehyde to DNPH and 100% recovery of the derivative. Variance in results is attributable to the use of an external standard for the analysis of these samples since a suitable internal standard for use with leachate had not been selected and evaluated when these analyses were performed.

only indicative of the formaldehyde concentrations that could be expected in the leachate from a landfill undergoing early stages of decomposition and not concentrations that may be present in leachate exposed to other environmental conditions. Continued investigations with the landfill cells as they proceed through the methane fermentation stage will help establish the ultimate fate of the formaldehyde presently detected in the leachate samples.

Preparation and Set-Up

To provide an opportunity to determine if the formaldehyde detected in landfill leachate was attributable only to the foam or also to other constituents in the solid waste, two additional bench-scale cells (19.0-liter metal containers) with the necessary appurtenances for moisture addition and leachate sample collection were constructed (November 1982). In one cell a 2.5-cm layer of foam was placed between two layers of shredded municipal solid waste; only shredded municipal solid waste was placed in the other cell. A total of 5.5 kg of solid waste was placed and compacted in each cell.

To expedite leachate generation, both cells were brought to apparent field capacity by the initial addition of 10 liters of distilled water. This water was added to the cells in small increments as the solid waste was placed and compacted in the cells to maximize uptake of moisture by the solid waste and minimize short-circuiting. Subsequent to the initial addition of water, the cells were sealed to prevent the further entry of air into the cells.

Operational and Sampling Procedures

Since the purpose of these tests was to determine if formaldehyde in leachate is attributable only to foam or also to other constituents of the solid waste, moisture addition to these cells was provided to insure that sufficient volumes of leachate would be generated for formaldehyde determination at periodic intervals.

Presentation and Discussion of Results

To date, only three samples have been collected from these cells. The results (Table 9) indicate that, although low concentrations of formaldehyde were present in the leachate from the cell containing foam (2.4 to 3.5 mg/l), trace amounts of formaldehyde were also present in the leachate from the cell that contained no foam (0.6 to 3.0 mg/l). However, since these experiments have only been in progress for approximately four weeks, the results are preliminary and should not yet be considered to be conclusively representative of typical leachate formaldehyde concentrations existing throughout the various stages of landfill stabilization.

TABLE 9. PRELIMINARY RESULTS OF THE DETERMINATION OF FORMALDEHYDE IN LEACHATES FROM BENCH-SCALE SIMULATED LANDFILL CELLS WITH AND WITHOUT FOAM

Date of Sample Collection	Formaldehyde Concentration, mg/l*		Comments
	Cell with Foam	Cell without Foam	
11/29/82	3.1	0.6	External standard used. (Distilled water spiked with formaldehyde to 500 ppb level)
12/14/82	3.5	3.0	Internal standard used. (Decachlorobiphenyl)
12/30/82	2.4	1.5	Internal standard used. (Decachlorobiphenyl)

*Determinations were made by derivatization of formaldehyde as 2,4-dinitrophenylhydrazone. Concentrations reported assume complete derivatization of formaldehyde to DNPH and 100% recovery of the derivative.

Leachability Tests

Because of the analytical interferences in the determination of formaldehyde in leachate, separate tests were also conducted to determine if formaldehyde can be extracted from the foam by immersion of the foam in distilled water and in 1% acetic acid solutions. The acetic acid solution was adopted to simulate conditions characteristic of landfill leachates during acid fermentation.

Experimental Procedure. The procedure utilized for these tests was based on a similar test conducted for SaniFoam, Inc. by the American Standards Testing Bureau, Inc., New York, New York in April 1982.[6] This procedure is summarized as follows:

> Two hundred and fifty (250) cm^3 of SaniFoam plastic foam (10 cm x 10 cm x 2.5 cm) were crumbled and placed in a clean cheese cloth. The foam was then immersed in 500 ml of solution (either distilled water or 1% acetic acid) and compressed five times. [Five hundred (500) ml were used during these tests as compared with 2000 ml used by the American Standards Testing Bureau, Inc. in order to be more representative of a typical rainfall event, i.e., 500 ml equates to a 5-cm rainfall onto a 100 cm^2 area, and yet produces sufficient liquid volume to saturate the foam.] Samples of the solution were then collected and analyzed for formaldehyde immediately and at selected ensuing time intervals.

Presentation and Discussion of Results. Samples were collected at periodic intervals and analyzed for formaldehyde using the chromatropic acid method. These results are presented in Table 10. The initial sample collected was also analyzed using direct aqueous injection, GC-MS which indicated the absence of formaldehyde in the sample at a level higher than 100 mg/1 (see Figures 26 and 27).

The chromatropic acid colorimetric method, which is capable of detecting low concentrations of formaldehyde, indicated the presence of formaldehyde (assuming that the color development was solely attributable to formaldehyde) in both the distilled water and acetic acid solution. Furthermore, the concentrations increased with time and were consistently higher in the acetic acid solution than in the distilled water. Higher concentrations would be expected with increased time as leaching of constituents from the foam continues until an equilibrium with the solution is reached and more so in the acetic acid solution where the more acidic conditions would tend to increase the leachability of constituents from the foam.

Caution must be used in the interpretation of these results, since the chromatropic acid method is susceptible to interferences (see Table 2). While the presence of constituents in the distilled water rinsing solutions that could result in a positive reaction with the reagent is unlikely, it is likely that the color development with the reagent can be attributable to compounds other than formaldehyde that are present in the foam and capable of being leached under the experimental conditions imposed. This assertion can be partially substantiated by the results of the analyses performed on samples from the subsequently discussed percolation tests. These results indicated significant differences between the concentrations measured by the chromatropic acid and the DNPH derivatization method. The apparent higher

TABLE 10. RESULTS OF THE FORMALDEHYDE LEACHABILITY TESTS CONDUCTED WITH SANIFOAM PLASTIC FOAM

Time of Sample Collection After Immersion of Foam	Time of Sample Analysis after Collection of Sample	Formaldehyde Concentration, mg/l*		Comments
		Foam in Distilled Water	Foam in 1000 mg/l Acetic Acid	
Initial Sample	Immediately	11***	13	Constituents of the foam that produce a positive reaction with the chromatropic reagent are being leached from the foam and are continuing to be so after 16 days (equilibrium between the constituents and solutions has not yet been reached). Whether color development is solely attributable to formaldehyde cannot be positively determined. It is likely that color development can be attributed to the reaction of the reagent with other constituents in the foam.
1 hour	Immediately	17	20	
	After 24 hours	17	16	
21 hours	Immediately	35	41	
	After 24 hours	27	52	
100 hours	Immediately	--**	--**	
	After 42 hours	97	192	
	After 282 hours	15	216	
150 hours	Immediately	128	300	
	After 240 hours	144		
380 hours	Immediately	254	>500 (595)**	

*Assumes color development is only attributable to formaldehyde.
**Adsorbance beyond range of standard curve.
***The results of the initial sample are consistent with those reported in a similar test conducted by American Standards Testing Bureau, Inc.[6]

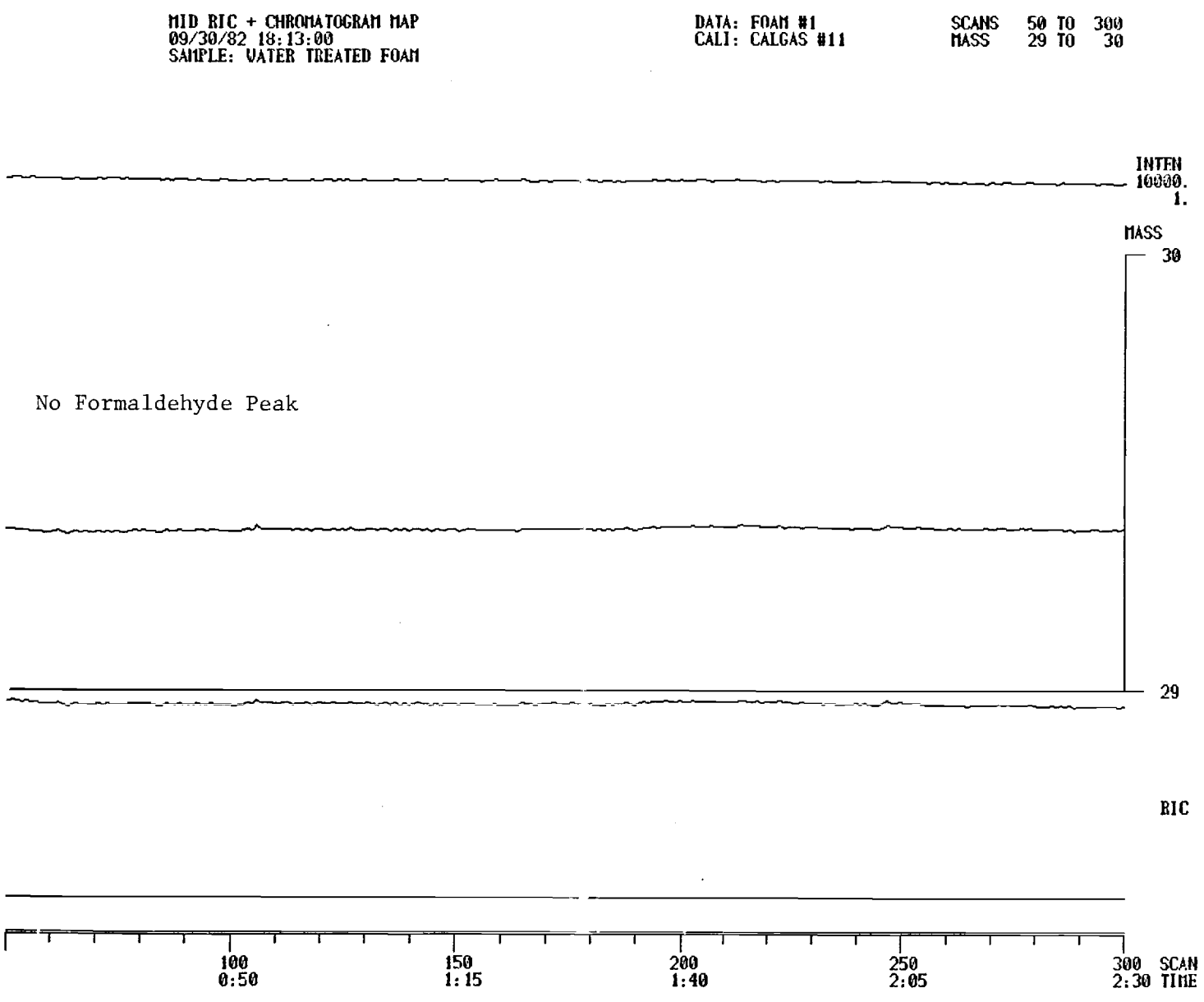

Figure 26. Fragmentogram of Formaldehyde in Distilled Water Immediately after Immersion of Foam.

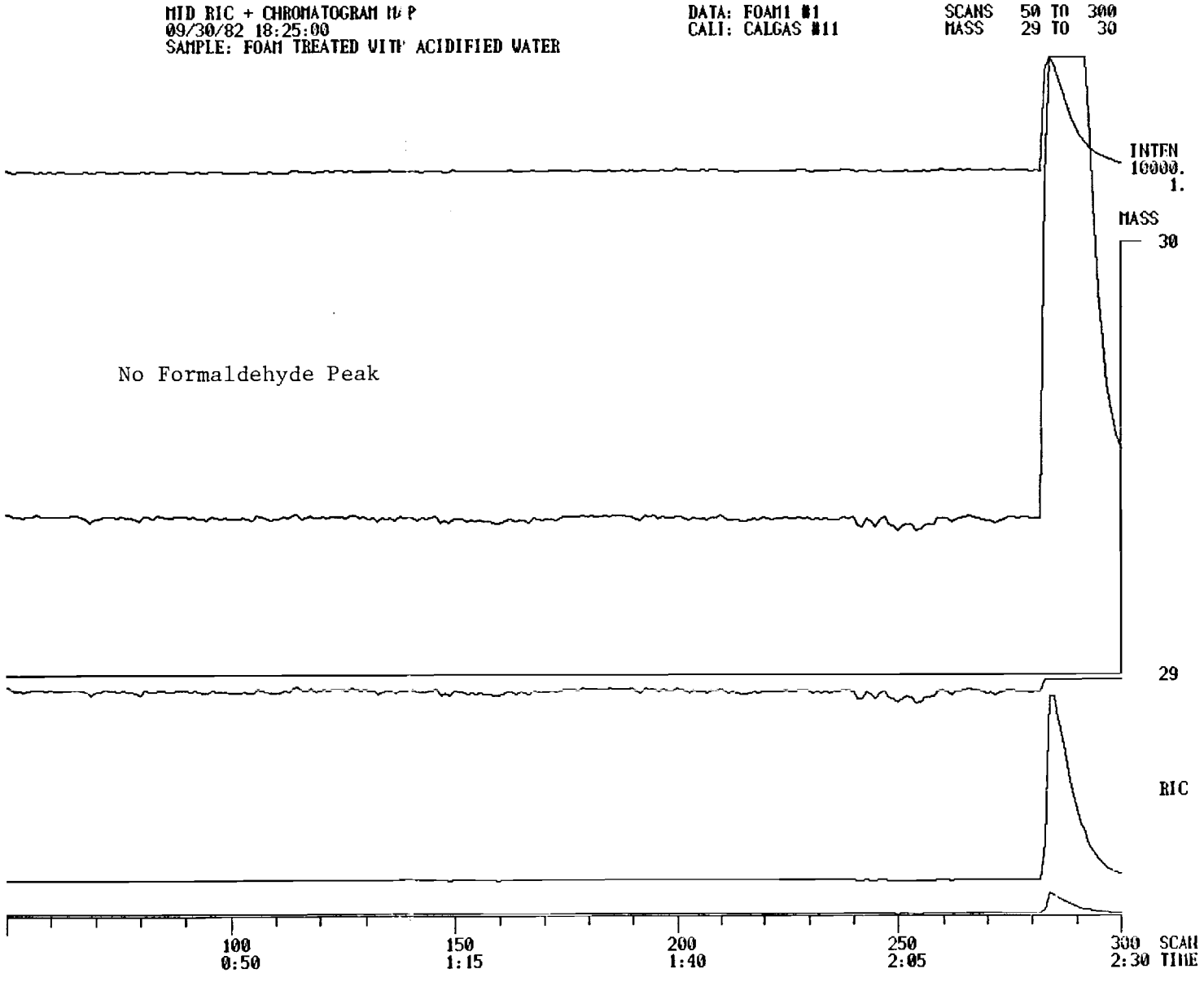

Figure 27. Fragmentogram of Formaldehyde in 1000 mg/l Acetic Acid Solution Immediately after Immersion of Foam.

concentrations measured by the chromatropic acid method are likely attributable to the additional color development resulting from the reaction of the chromatropic acid reagent with other constituents of the foam. Hence, these results were considered inconclusive because of the interferences from other constituents present in the foam. (Further analysis of these solutions by the DNPH derivatization method was not accomplished, since the leachability tests had been concluded prior to the development of this method.)

Percolation Tests

To determine if formaldehyde could be leached from the foam by the percolation of water through the foam, percolation tests were also conducted.

Experimental Procedure. The procedure used for these tests consisted of percolating 200 ml of distilled water (the equivalent of a 2.5-cm rainfall) through a 2.5-cm thick layer of foam (surface area 78-cm^2) placed between two layers of gravel in a Buchner funnel (10-cm diameter). The liquid collected after percolating through the Buchner funnel was analyzed for formaldehyde. As a control, distilled water was also percolated through a Buchner funnel containing only gravel, with the percolate being similarly collected and analyzed for formaldehyde.

Presentation and Discussion of Results. The results of the percolation tests are presented in Table 11. The significant differences in the concentrations measured by the chromatropic acid method as compared with the DNPH derivatization method could be attributed to the reaction of the chromatropic acid reagent with constituents of the foam other than formaldehyde and further substantiate the previous assertions concerning the limitations on the use of the chromatropic acid colorimetric method.

TABLE 11. RESULTS OF PERCOLATION TESTS CONDUCTED WITH SANIFOAM PLASTIC FOAM

Date of Test	Time Analysis Was Performed After Conduct of Test	Formaldehyde Concentration, mg/l	Analytical Method Used	Comments
10/05/82	Immediate	-*	Chromatropic Acid	
	24 hours later	60**	Chromatropic Acid	
10/06/82	Immediate	174**	Chromatropic Acid	The same foam as used on 10/05/82 was used for this test.
11/27/82	Immediate	2.3 ± 1.7	Derivatization of formaldehyde as DNPH	

*Analytical instrumentation problems prevented immediate analysis on 10/05/82.
**Assumes all color development was attributable to the presence of formaldehyde.

Note: Samples analyzed from the control without foam indicated the absence of formaldehyde.

However, as the DNPH method is not subject to such interferences and is specific for formaldehyde, the results indicate that formaldehyde can be extracted from the foam by the percolation of water through the foam. As only a small quantity (200 ml) of water was percolated through the foam layer, it cannot be determined if formaldehyde would continue to be extracted from the foam with additional rinsings. Further percolation tests to determine how much formaldehyde can be extracted from the foam will be conducted in subsequent phases of this research project.

CONCLUSIONS

From the research efforts to date, the following preliminary conclusions can be drawn.

1. Derivatization of formaldehyde as 2,4-dinitrophenylhydrazone (DNPH) followed by the extraction and concentration of the derivative in an organic solvent and subsequent analysis by capillary column GC is a viable method for the determination of formaldehyde in complex aqueous solutions.

2. The simulated landfill cells are presently undergoing early stages of microbially mediated decomposition of the solid waste ingredients with associated high pollutant concentrations and low pH in the leachate and a minimal gas production. Continued operation of the landfill cells through methane fermentation will be necessary to ascertain the ultimate fate of the formaldehyde associated with the foam added initially to the cells with the solid waste.

3. The low concentrations (3.3 to 14.3 mg/l) of formaldehyde present in the leachate from the single-pass cell are indicative of the formaldehyde concentrations that could be expected to exist in the leachate within a similarly operated landfill undergoing early stages of decomposition, but do not necessarily reflect the concentrations that could be expected to be present in leachates throughout the total period of stabilization within the landfill as it progresses from the acid fermentation through the methane fermentation phases.

4. Formaldehyde detected in leachate can originate from constituents present in solid wastes.

5. Formaldehyde can be extracted from the foam by immersion or percolation of water or other aqueous solutions through the foam.

APPENDIX A

ANALYTICAL METHODS FOR THE DETERMINATION OF FORMALDEHYDE IN AQUEOUS SOLUTIONS

A. Chromatropic Acid Method for the Determination of Formaldehyde in Aqueous Solutions*

1. Reagent Preparation: Dissolve 2.5 g of dry powdered chromatropic acid in 25 ml of distilled sater and filter to obtain a clear solution.

2. Procedure:

   a) Place 0.5 ml of sample in a 50-ml glass-stoppered volumetric flask.

   b) Add 0.5 ml of chromatropic acid reagent followed by the gradual addition of 5 ml of concentrated sulfuric acid with continuous shaking.

   c) Stopper flask and place in boiling water for 30 minutes. Cool and dilute to 50 ml, cool again and readjust volume to 50 ml if necessary.

   d) Read adsorbance on a spectophotometer at a wavelength of 570 millimicrons.

B. Gas Chromatographic Method for Determination of Formaldehyde in Aqueous Solutions

1. Instrument: Perkin Elmer Sigma 3.

2. Experimental Conditions:

   a) Injection mode; on column

   b) Injector temperature; 250°C

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*Walker, J. F., Formaldehyde, 3rd Ed., Reinhold, New York, 1964.

c) Column; 1) Porapax G 60/80 mesh

2) Porapax T 60/80 mesh, glass column 1.83 m long, 2 mm I.D.

d) Oven Temperature Program; 130°C (5 min) - 5°/min - 150°C (1 min)

e) Volume Sample Injected; 1.0 microliter

C. Gas Chromatographic-Mass Spectroscopy (GC-MS) Method for Determination of Formaldehyde in Aqueous Solutions

1. Instrument (GC): Hewlett Packard 5830 A GC

2. Experimental Conditions (GC):

a) Injection mode; split mode (split ratio 50:1)

b) Injector temperature; 250°C

c) Column; glass capillary 30 m x 0.35 mm I.D., carbowax 20 M

d) Oven Temperature Program; 40°C (0.2 min) - 20°C/min - 230°C

e) Volume Sample Injected; 1.0 microliter

f) Transfer Line; fused silica tubing 0.2 mm I.D.

3. Instrument (MS): Finnigan 4023 MS and Nova 3 Data System

4. Experimental Conditions (MS):

a) Ionization Mode; Electron Impact

b) Electron Energy; 70 eV

c) Emission Current; 0.5 mA

d) Electron Multiplier; 1450 V

e) Multiple Ion Detection; m/e 29 and 30

APPENDIX B

2,4-DINITROPHENYLHYDRAZONE (DNPH) DERIVATIVE METHOD FOR THE DETERMINATION OF TRACE AMOUNTS OF FORMALDEHYDE

1. Reagent Preparation

   Dissolve 0.25 g of 2,4-dinitrophenylhydrazine (DNP) in 100 ml of 6 M hydrochloric acid.[5]

2. Glassware Preparation

   All glassware must be cleaned and prepared by the standard techniques used for trace organic analysis.

3. Procedure

   a) To 100 ml of sample, add 5 ml of DNP reagent.

   b) Mix the sample with a magnetic stirrer for 5 minutes and then add 50 ml of methylene chloride.

   c) Continue mixing for 1.5 hours.

   d) Place the solution in a separatory funnel and separate the organic solvent from the aqueous solution.

   e) Perform the extraction two more times with 50-ml aliquots of methylene chloride.

   f) Concentrate the organic solvent to approximately 4 ml with a Kuderna Danish apparatus at 70°C and finally to 1 to 1.5 ml by gentle drying with nitrogen.

   g) Analyze the sample by gas chromatography.

4. Gas Chromatographic Conditions

   a) Instrument; Hewlett Packard 5830A equipped with capillary injection port.

   b) Injection Mode; splitless.

c) Injector Temperature; 250°C.

d) Column; Gas capillary, 0.3 mm I.D., 30 m long coated with SE-54.

e) Oven Temperature Program; 40°C (2 min) - 15°/min - 290°C (5 min).

f) Sample Volume Injected; 0.5 microliter.

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E-20-H01

SCEGIT
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FINAL REPORT

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Submitted to

SANIFOAM, INC.
COSTA MESA, CALIFORNIA

by

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GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

December 1983

GEORGIA INSTITUTE OF TECHNOLOGY
A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA
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EXECUTIVE SUMMARY

The use of plastic foam has gained recent popularity as an alternative cover material because of its ease and homogeneity of application; its ability to increase otherwise unavailable landfill capacity and, thereby, extend service life; and its frequent economic advantage when compared to the costs of acquisition of other cover materials. In the case of SaniFoam plastic foam, results of preliminary studies on its nature and general applicability in landfilling operations have been promising, however, they have not adequately addressed the relatively long-term issues of ultimate fate and environmental impact, i.e., the impacts of foam and its leachable constituents on the landfill environment and vice versa. Consequently, this research project was initiated to help assess the relative suitability and/or potential applicability of SaniFoam plastic foam as an alternative cover material during landfill disposal of solid wastes, with special emphasis on the extent and impact of formaldehyde leaching during landfill stabilization.

Since the accurate monitoring of formaldehyde was considered essential in attaining the goals of this project, several analytical methods were evaluated for the determination of formaldehyde concentrations in leachate samples. All were found to have limitations which ultimately restricted their use particularly for trace concentrations of formaldehyde. A subsequent review of the literature revealed that several investigators had successfully used the derivatization of 2,4-dinitrophenylhydrazone from the reaction of carbonyl compounds with

2,4-dinitrophenylhydrazine to determine trace amounts of aldehydes and other carbonyl compounds. The application of this analytical approach resulted in the development of a new analytical protocol for the determination and quantification of formaldehyde in leachate which was subsequently used during the major part of this investigation.

To provide an opportunity to assess the potential impact of formaldehyde leaching from foam during landfill stabilization, two simulated landfill cells with necessary appurtenances to permit leachate and gas collection for a "single-pass" cell as well as leachate recycle for a "recycle cell" were constructed. The single-pass cell was intended to simulate the impact of rainfall during conventional landfill operations; the recycle cell was intended to simulate conditions where rainfall induced leachate was contained, collected and recycled, thereby using the landfill as an *in situ* leachate treatment system. In both cells, a 2-inch (5-cm) intermediate layer of foam was placed between two layers of shredded residential-type solid waste (2.8 g of foam/dry kg of solid waste).

After sealing the cells to the atmosphere, moisture was added to initially bring them to field capacity and to subsequently simulate rainfall events in the Atlanta area. Accumulated leachate was collected and recycled in the recycle cell and collected and removed to storage from the single-pass cell. Leachate and gas samples were collected at periodic intervals and analyzed to determine the progression of landfill stabilization processes within the cells. In addition, the volume of gas generated and temperatures were recorded on a daily basis for both landfill systems. As the investigations progressed the cells were

seeded with digested sludge to establish a viable microbial methanogenic population within the cells.

Results from these studies indicated that 18.4 mg of formaldehyde per gram of foam placed in the single-pass cell were removed with the leachate as other solid waste components were extracted without significant conversion or stabilization. Similar quantities of formaldehyde (16.5 mg/g of foam) were extracted from the recycle cell. However, because of the more rapid and complete stabilization of the solid waste present in the recycle cell, formaldehyde concentrations in the recycled leachate decreased from approximately 42 mg/ℓ to 3 mg/ℓ, thereby indicating that conditions were more favorable, particularly during the methane fermentation phase of stabilization, for the anaerobic microbial utilization and conversion of formaldehyde.

Because of the widespread use of products containing formaldehyde-based resins (e.g., pressed wood products, insulation, paper, fabric, carpet), many of which are eventually also disposed of in landfills, it was suspected that some of the formaldehyde removed from the cells during the research investigations originated from constituents in the solid waste. Therefore, to determine the relative contribution of formaldehyde detected in the leachate samples from the simulated landfill cells attributable to the foam as compared to other solid waste constituents, leachability studies were also conducted using two additional bench-scale simulated landfill cells with the necessary appurtenances for moisture addition and leachate sample collection. In one cell, a one-inch (2.5-cm) layer of foam was placed between two layers of shredded residential-type solid waste; only shredded waste

was placed in the other cell. Moisture was added to both cells after sealing to generate leachate at periodic intervals. Leachate samples collected from these cells were again analyzed and characterized by selected indicator parameters. Results from this complementary study indicated that some of the formaldehyde detected in the leachate originated from the solid waste itself. With similar removals of formaldehyde from solid waste in an actual landfill, approximately 25 percent of the total mass of formaldehyde leached from conventional landfill cells covered with foam could originate from the solid waste.

To confirm the absence of inhibition of landfill stabilization and associated methane fermentation processes by the formaldehyde as well as other constituents leached from the foam, two batch digestors with appurtenances for substrate addition, sludge removal and gas production monitoring were constructed. After seeding with fresh digested sludge, one digestor received no subsequent addition of substrate so that gas produced and attributable only to the degradation of organic matter already present in the sludge could be measured; the other test digestor received daily additions of leachate collected from the single-pass simulated landfill cell as a sole source of substrate. Following an initial acclimation period during which loadings to the test digestor were gradually increased, leachate addition was maintained at a constant loading rate. Samples of the leachate used as a substrate and supernatant from this digestor were collected at periodic intervals and analyzed for parameters indicative of digestor performance. In addition, the volume of gas generated by the digestors was monitored as was the composition of the gas. Results from this study substantiated the previous findings with the recycle

cell that formaldehyde was biodegradable under anaerobic conditions. Futhermore, leachate generated from the simulated landfills containing foam did not appear to contain other constituents inhibitory to methane fermentation processes.

The overall results of these studies indicated that: i) the derivatization of formaldehyde as 2,4-dinitrophenylhydrazone is a viable method for determination of formaldehyde in leachate; ii) the total mass of formaldehyde removed from the recycle and single-pass simulated landfill cells containing 2.8 g of foam/dry kg of solid waste was determined to be 16.5 and 18.4 mg/ g of foam, respectively, over the 500-day study period; iii) some of the formaldehyde detected in the leachate originated from the solid waste and with similar removals of formaldehyde from solid waste in an actual landfill, approximately 25 percent of the total mass of formaldehyde leached from conventional landfill cells covered with foam could originate from the solid waste; iv) formaldehyde and other possible constituents leached from the foam did not preclude the anaerobic microbial production of methane during landfill stabilization; and, v) degradation of formaldehyde occurred during the methane fermentation phase of landfill stabilization and this process was accelerated by utilizing leachate recycle as an *in situ* treatment method. Consequently, SaniFoam plastic foam may be used as an alternate to daily landfill cover without posing adverse environmental impacts attributable to the release of formaldehyde from the foam.

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INTRODUCTION

Background

Sanitary landfills are the most common method of municipal solid waste disposal in the United States, primarily due to economic advantages over other solid waste management alternatives. In the overall planning design and operation of sanitary landfills, requirements for daily, intermediate and final cover often impose a costly and problematic element. Moreover, availability and suitability of cover soils often dictate whether landfilling operations can be cost effective. Although soil is often required for intermediate and final cover in order to maintain structural integrity and to support surface vegetation, the use of alternative daily cover materials may be more advantageous and economical in many applications.

The use of plastic foam has gained recent popularity as an alternative cover material because of its ease and homogeneity of application, its ability to increase otherwise unavailable capacity and thereby extend service life, and its frequent economic advantage over alternative cover methods. In the case of SaniFoam plastic foam, efforts have been initiated to determine its nature and general applicability in landfilling operations. [1-3] Although the results of these preliminary studies appear promising, they did not adequately address the relatively long-term issues of ultimate fate and environmental impact, i.e., the impacts of foam and its leachable constituents on the landfill environment and *vice versa*. Hence, the leaching of constituents from the foam (e.g., formaldehyde) during and after landfilling operations is a crucial issue relating not only to the effectiveness of the foam in performing its intended purpose

without hazard, but also to the acceptability of the foam within a process assessment and regulatory perspective.

Preliminary Considerations

Most sanitary landfills proceed through a series of relatively predictable microbially mediated events, the significance and longevity of which are dependent upon various factors such as, climatological conditions, operations variables, management options and control factors operative or being applied either externally or internally to the landfill. With the recognition that a landfill functions throughout much of its active life as an anaerobic microbial process, analogous in concept to a batch anaerobic digestor, certain performance related and time dependent concepts can be identified. Hence, following an initial lag or adjustment which is normally coupled with the development of a viable microbial population, the process of landfill stabilization can be illustrated by several more or less discrete and sequential phases, each varying in intensity and longevity according to the prevailing operational condition. For example, the following five stabilization phases may be identified in terms of principal events occurring during each:[4]

Phase I: Initial Adjustment

The period from initial refuse placement through preliminary moisture accumulation, subsidence and closure of a landfill area, to the point at which changes in environmental parameters are first detected to reflect the onset of stabilization processes which are trending in a logical fashion.

Phase II: Transition

The period during which field capacity is exceeded and leachate is formed, a transition from initial aerobic to anaerobic microbial

stabilization occurs, the primary electron acceptor shifts from oxygen to nitrates and sulfates with the displacement of oxygen by carbon dioxide in the gas, a trend toward reducing conditions is established, and measurable intermediates such as the volatile organic acids first appear in the leachate.

Phase III: Acid Formation

The period during which intermediary volatile organic acids become predominant with the continuing hydrolysis and fermentation of refuse and leachate constituents, a precipitous decrease in pH occurs with a concomitant mobilization and possible complexation of metal species, nutrients such as nitrogen and phosphorus are released and utilized in support of the growth of biomass commensurate with the prevailing substrate conversion rates, and hydrogen may be detected and affect the nature and type of intermediary products being formed.

Phase IV: Methane Fermentation

The period during which the intermediary products appearing during the acid formation phase are converted to methane and excess carbon dioxide, the pH returns from a buffer level controlled by the volatile organic acids to one characteristic of the bicarbonate buffering system, oxidation-reduction potentials are at their lowest values, nutrients continue to be consumed, complexation and precipitation of metal species proceed, and leachate strength is dramatically decreased in correspondence with increases in gas production.

Phase V: Final Maturation

The period of relative dormancy following active biological stabilization of the readily available organic constituents in the refuse and leachate during which nutrients may become limiting, measurable gas production ceases, natural environmental conditions become

reinstated, oxygen and oxidized species slowly reappear with a corresponding increase in oxidation-reduction potential, and more microbially resistant organic materials may be slowly converted with the possible production of humic-like substances capable of complexing with and re-mobilizing heavy metals.

The accompanying changes in leachate and gas quality that occur as a landfill proceeds through these phases of stabilization may be illustrated as in Figure 1 where certain indicator parameters or indices may be used to detect and describe the presence, intensity and longevity of each phase of landfill stabilization. Normally, these processes occur over extended periods of time which makes analysis and interpretation of events, especially those that occur in the latter phases, difficult and often impractical. However, by collecting and recycling leachate through the wastes, these processes can be made to occur in a more predictable fashion and within a more manageable time frame. Consequently, this leachate recycle strategy compared with single-pass operation which is representative of conventional landfill management practices, was used as an experimental technique to accelerate exposure of the foam to various environmental conditions within the landfill and thus enable assessment of the potential impact of formaldehyde and possible other constituents leached from the foam during the overall progress of landfill stabilization processes.

Objectives and Research Efforts

Based upon the background information and preliminary considerations, this research project was initiated to assess the relative suitability and/or potential applicability of SaniFoam plastic foam as a cover material during landfill operations, with

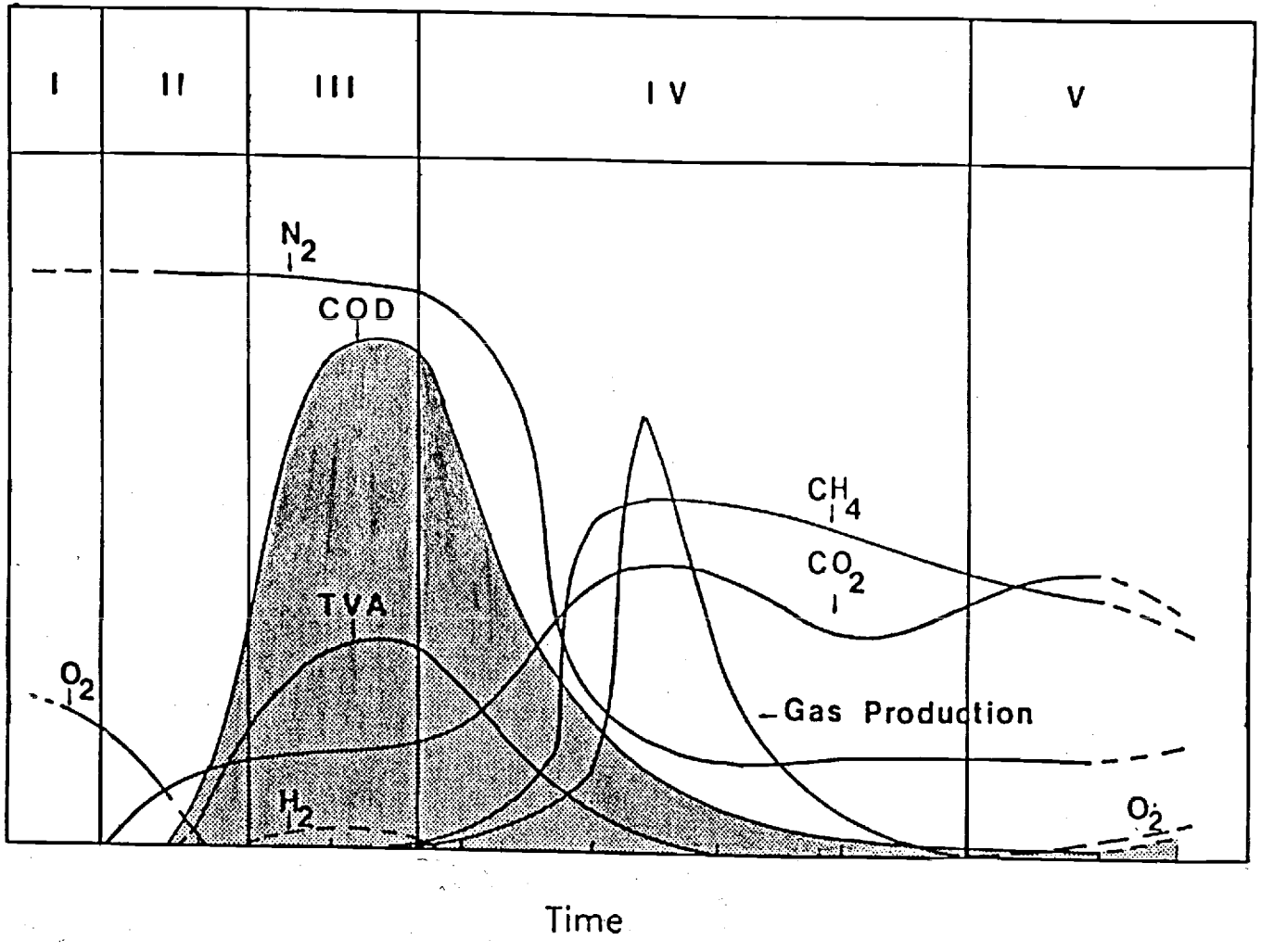


Figure 1. Changes in Selected Indicator Parameters During the Phases of Landfill Stabilization. (After Pohland, 1983)

special emphasis on the fate and impact of leached formaldehyde on landfill stabilization processes and the environment. To accomplish this objective, research efforts were directed toward the development of an analytical method specific for the determination and quantification of formaldehyde in leachates, assessment of the potential impact and fate of formaldehyde within the landfill environment when combined with natural processes of stabilization and gas production, determination of the relative contribution of formaldehyde to leachate from the foam when compared to other constituents present in the solid waste, and evaluation of the biodegradability of formaldehyde present in the leachate by anaerobic processes as well as the possible inhibition to anaerobic degradation due to other constituents contributed by the foam.

EXPERIMENTAL STUDIES

Analytical Method Development for Determination and Quantification of Formaldehyde in Leachates

Although there exist several established analytical methods for the measurement of formaldehyde in air,[5,6] little research has been performed to determine aldehydes in contaminated aqueous solutions and no standard analytical method has been developed for the measurement of formaldehyde in complex aqueous waste samples such as leachates. Therefore, several analytical methods were evaluated for the analysis of formaldehydes in leachate samples. These included: i) the chromotropic acid colorimetric technique; ii) a direct aqueous injection, packed column Gas Chromatographic (GC) technique; and, iii) a direct aqueous injection, glass capillary column Gas Chromatographic - Mass Spectroscopic (GC-MS) technique. All of these methods, however, were found to have limitations (Table 1) which ultimately restricted their use for the determination of trace amounts of formaldehyde in leachate samples originating from landfill disposal of solid wastes.

A review of the literature indicated that several investigators [7-9] have successfully used derivatization techniques prior to gas chromatographic (GC) or high pressure liquid chromatographic (HPLC) analysis for the determination of trace amounts of aldehydes and other carbonyl compounds. Mansfield, et al.,[7] successfully used the formation of 2,4-dinitropheylhydrazone (DNPH) from the reaction of formaldehyde with 2,4-dinitrophenylhydrazine (DNP) to detect formaldehyde in tobacco smoke. Fung and Grosjean [8] as well as Selin [9] have

Table 1. Limitations of Analytical Methods for the Determination of Formaldehyde in Complex Aqueous Solutions

Method*	Limitations
Chromotropic Acid Colorimetric Method	Although this method has been effectively used to detect low concentrations of formaldehyde with good accuracy, the reliability of the method decreases when used with complex mixtures (e.g., leachate) due to the presence of other compounds in the solution that can interfere with the formation and/or intensity of color. Compounds which can cause such interferences include acetaldehyde, acrolein, beta-hydroxpropionaldehyde, methyl ethyl ketone and diacetone alcohol. Some of these compounds or others are likely to be present in many landfill leachates. In addition, the natural color of the leachate masks normal color development, thereby further complicating the use of this method.
Direct Aqueous Injection Gas Chromatographic Technique	Direct aqueous injection GC methods have been used for determination of relatively high concentrations of formaldehyde in simple aqueous solutions. However, this method did not provide the degree of peak separation considered requisite for reliable analyses with leachate samples.
Direct Aqueous Injection Gas Chromatography-Mass Spectroscopy (GC-MS) Technique	Although capillary columns and GC-MS are more reliable for determining the presence or absence of formaldehyde, concentration levels below 100 mg/l in aqueous solutions could not be detected.

*Analytical methods and/or experimental conditions for these methods are presented in more detail in Appendix A.

similiarly used the derivatization to DNPH's to separate and quantify nanogram amounts of carbonyl compounds.

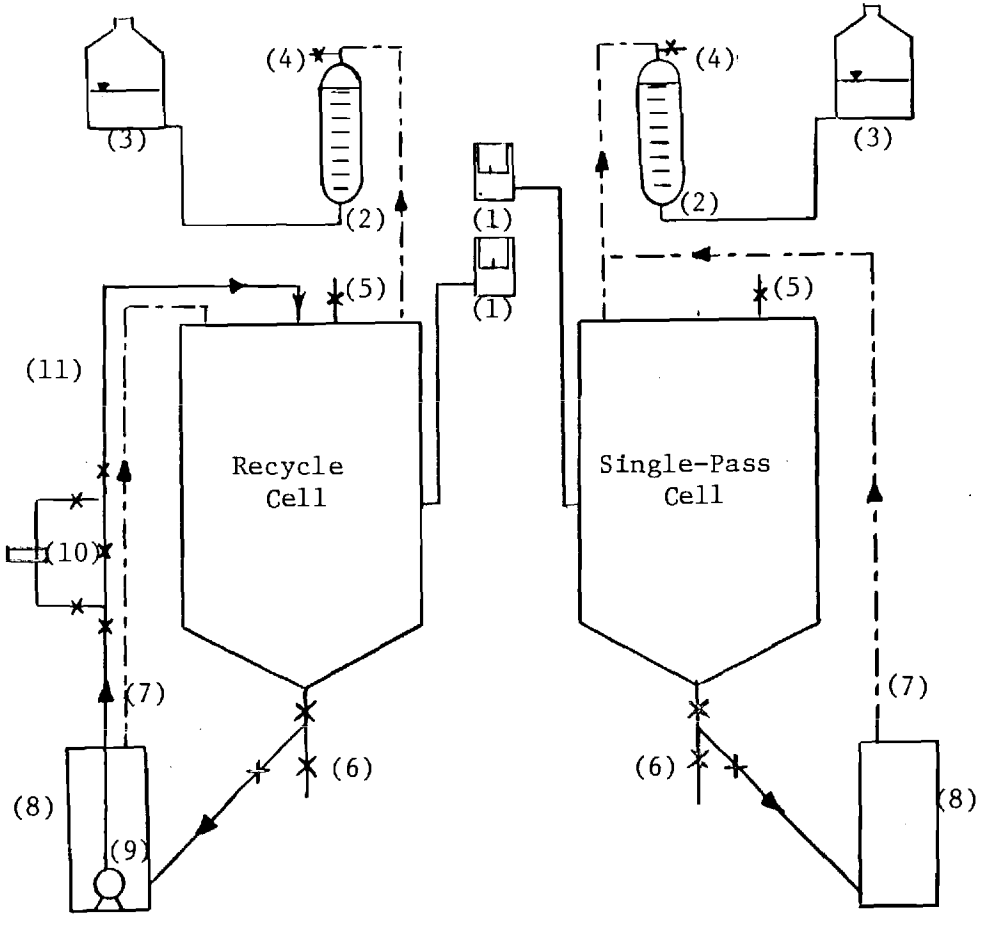
Although none of the investigators have applied these techniques to complex aqueous solutions, use of this derivatization technique appeared feasible for the specific determination and quantification of formaldehyde in leachate samples. Consequently, analytical method development was initiated as part of this research initiative to take advantage of the reaction of carbonyl compounds with 2,4-dinitrophenylhydrazine (DNP) and subsequent formation of the derivative, 2,4-dinitrophenylhydrazone (DNPH), according to the reaction:

$$RR'C=O + NH_2NHC_6H_3(NO_2)_2 \rightarrow RR'C=NNHC_6H_3(NO_2)_2 + H_2O$$

Therefore, the resultant analytical method consisted of: i) derivatization of formaldehyde with an excess of 2,4-dinitrophenylhydrazine in acidic solution for approximately 1.5 hours to form 2,4-dinitrophenylhydrazone (DNPH); ii) liquid-liquid solvent extraction of the aqueous solutions with methylene chloride; iii) concentration of the extract by Kuderna-Danish Apparatus; and, iv) subsequent analysis by glass capillary column GC-FID. This method is described in more detail in Appendix B.

Landfill Simulation Studies

To provide an opportunity to assess the potential impact of formaldehyde that could be leached from the foam during its use as a cover material during landfill operations, two simulated landfill cells with necessary appurtenances to permit leachate and gas collection for the single-pass cell as well as leachate recycle for the recycle cell were constructed as represented in Figures 2 and 3. The single-pass cell was intended to simulate the impact of rainfall induced leaching events during conventional landfill operations; the recycle



KEY

(1) Temperature Recorder
(2) Gas Collecting Buret
(3) Leveling Bottle
(4) Gas Release Valve
(5) Water Addition Port
(6) Leachate Drain Pipe/ Sampling Port
(7) Leachate Reservoir Gas Line
(8) Leachate Reservoir
(9) Leachate Recycle Pump
(10) pH/ORP Measuring Loop
(11) Leachate Recycle Line

Figure 2. Schematic Diagram of the Simulated Landfill Cells

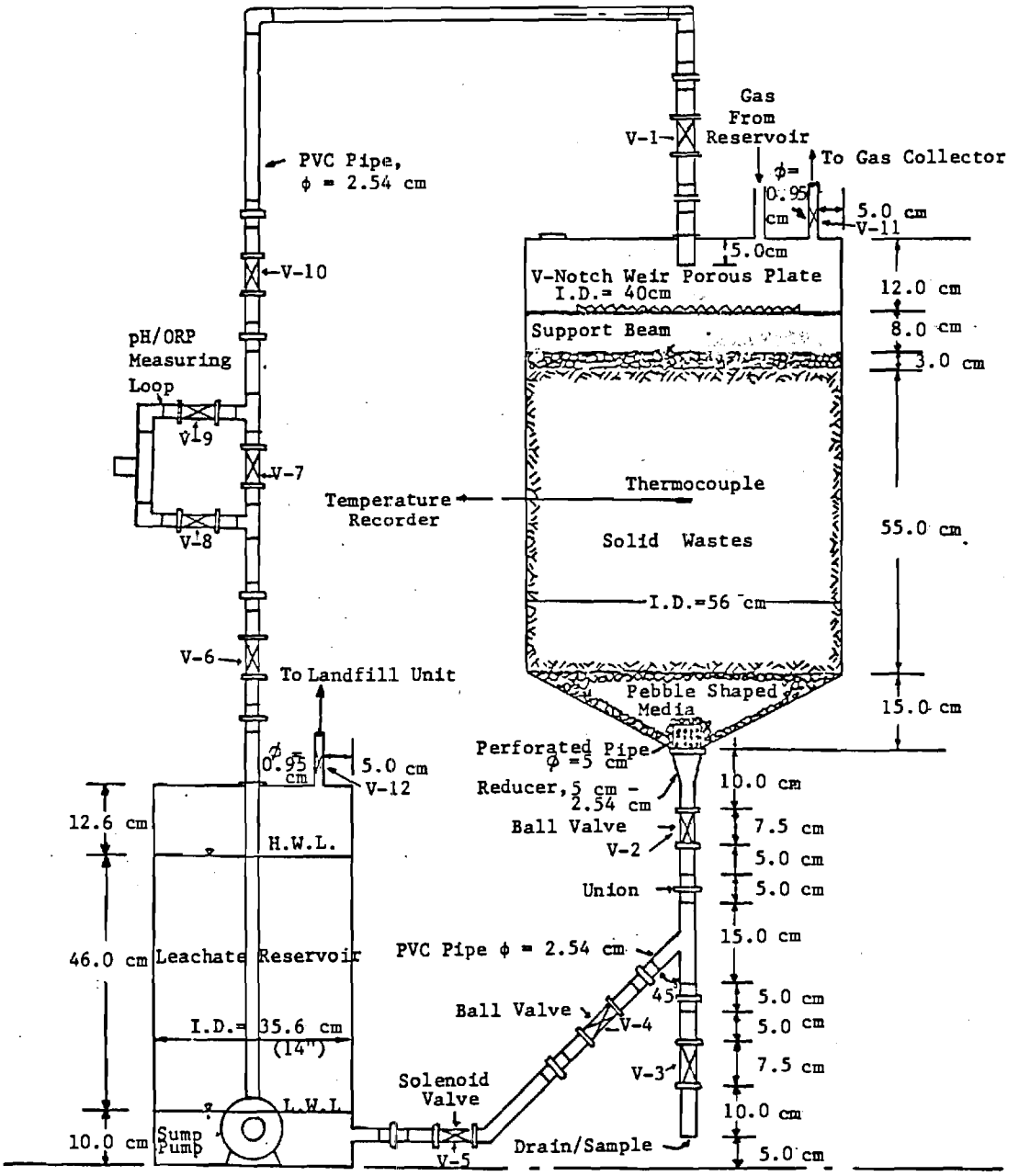


Figure 3. Detailed Drawing of Landfill Cell with Leachate Recycle

cell was intended to simulate conditions where leachate is formed, contained, collected and recycled, thereby using the landfill as an *in situ* leachate treatment system.

Simulated Landfill Cell Preparation. To initiate the simulated landfill studies, a layer of shredded residential-type solid waste was added to both cells, manually compacted, and covered by spraying with a 5-cm layer of SaniFoam plastic foam which was allowed to cure overnight. Both the manner in which the foam was applied (e.g., spray nozzle) and the thickness of layer were reflective of actual procedures presently being used at landfills. The foam layer was then broken into small (5-cm) fragments and a second layer of compacted solid waste was added to each cell. As the solid waste was being placed into the cells, samples of the waste were collected for subsequent characterization. A total of 60kg (39kg dry weight) of solid waste and approximately 2.8 g of foam/dry kg of solid waste were placed in each cell.

In order to bring the cells to apparent field capacity and expedite the generation of leachate, 34 liters of distilled water were added to each cell. To minimize short-circuiting, the water was added in small increments and distributed evenly across the surface of the solid waste over a two-day period. Following this initial addition of water, the cells were sealed to prevent the entry of air and to allow for the collection of gases generated within each of the cells throughout the study period.

Operational Procedures. After the cells were brought to apparent field capacity, additional moisture (distilled water) was added in amounts and at intervals corresponding to rainfall events in the

Atlanta, GA area. Information on rainfall was obtained from the meteorological station located on the Georgia Tech campus; data on moisture accumulations for both cells are presented in Table 2 and Figure 4. Moisture addition to the recycle cell was terminated on Day 62 as a sufficient volume of water had been accumulated in this cell to allow for leachate recycle, initiation of active landfill stabilization processes, and periodic sample collection and analysis.

Accumulated leachate was collected and recycled on a daily or weekly basis according to the schedule indicated in Figure 4 for the recycle cell, and collected and removed to storage in the case of the single-pass cell. In addition, the volume of gas generated and temperatures were recorded on a daily basis for both landfill systems.

Sludge Additions. In order to establish an active methanogenic microbial population within the cells and assure completion of the landfill stabilization processes within the time constraints of this study, digested sludge obtained from the Clayton Wastewater Treatment Plant in Atlanta was added to both cells. Four liters of sludge were initially added to both cells on June 16 (Day 340). This was followed by a subsequent addition of six liters on June 30 (Day 354) as there was little indication of methanogenic microbial activity (e.g., increased CH_4 production) after the initial addition of sludge. These sludge additions were considered necessary to initiate the methanogenic phase of stabilization, since the high volatile fatty acid content of the leachate and relatively homogeneous conditions particularly within the recycle cell tended to inhibit establishment of a viable methanogenic population within a reasonable time frame.

Sample Collection and Analysis. Collection of leachate samples

Table 2. Cumulative Moisture Addition to Recyle and Single-Pass Cells

Time, days	Cumulative moisture, liters		Time, days	Cumulative moisture, liters	
	Recycle Cell	Single-Pass Cell		Recycle Cell	Single-Pass Cell
1	34.0*	34.0*	222	-	91.40
8	38.0	38.0	232	-	92.90
9	42.23	42.23	243	-	93.40
13	46.23	46.23	260	-	95.40
14	47.38	47.38	272	-	96.90
16	48.68	48.68	285	-	98.40
17	51.26	51.26	310	-	100.40
19	54.26	54.26	337	-	101.90
20	57.26	57.26	340	85.10+	104.90+
35	58.00	58.00	341	-	108.90
37	62.00	62.00	345	-	110.70
39	62.60	62.60	354	-	112.20
45	63.10	63.10	355	91.10+	118.20+
48	63.60	63.60	359	-	119.20
52	67.60	67.60	363	-	119.70
54	71.60	71.60	376	-	121.20
55	73.60	73.60	381	-	122.70
62	77.10	77.10	393	-	124.20
121	79.10	79.10	409	-	125.20
129	80.10	80.10	430	-	126.70
136	81.10	81.10	441	-	128.20
146	-	82.10	457	-	129.70
157	-	83.60	458	-	130.20
166	-	84.60	469	-	131.70
189	-	85.60	478	-	133.20
207	-	87.10	485	-	134.20
208	-	88.10	495	-	135.70
215	-	89.60	506	-	137.20
219	-	90.60			

*Moisture added to bring cells to apparent field capacity.
+Digested sludge addition.

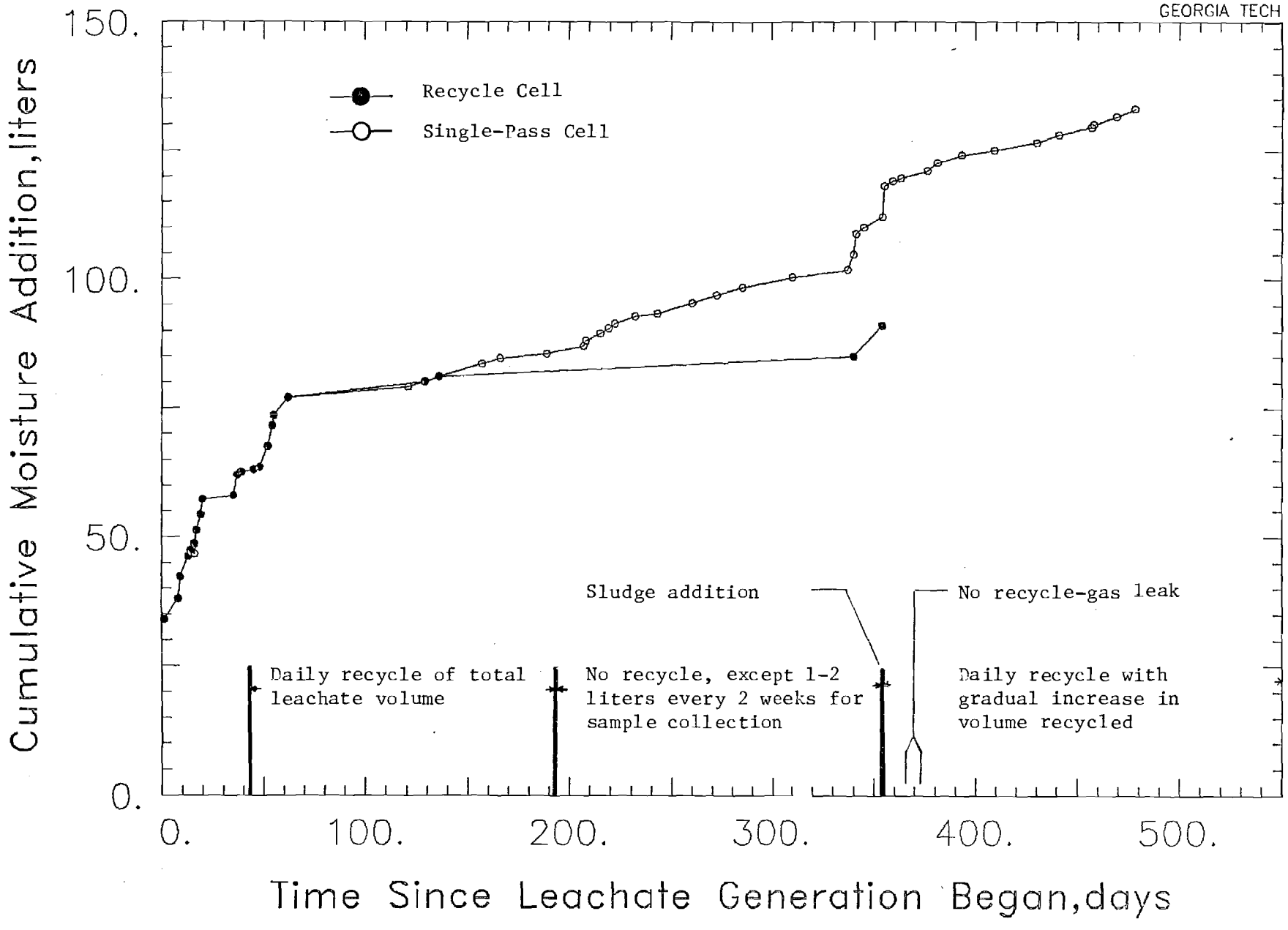


Figure 4. Cumulative Moisture Addition to Simulated Landfill Cells

for analyses was initiated when sufficient quantities of leachate were generated by the cells and continued at periodic intervals (approximately weekly) for the duration of the study. Samples of gases produced by the cells were also collected and analyzed at periodic intervals. These analyses were used to determine the progression of landfill stabilization processes within the cells. Analyses performed on leachate samples included: pH, Oxidation-Reduction Potential (ORP), conductivity, total alkalinity, volatile acids, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD_5), Total Organic Carbon (TOC), chlorides, sulfides, selected metals and formaldehyde. Gas samples were analyzed for relative composition of nitrogen, carbon dioxide, oxygen, hydrogen and methane. The analytical methods and instrumentation used for these analyses are summarized in Table 3.

Leachability Studies with Single-Pass Simulated Landfill Cells with and Without Foam.

Cell Construction. To provide an opportunity to determine if the formaldehyde detected in landfill leachate was attributable only to the foam or also to other constituents in the solid waste, two additional bench-scale simulated landfill cells (19.0-liter metal containers) with the necessary appurtenances for moisture addition and leachate sample collection were constructed. In one cell, a 2.5-cm layer of foam (10 g) was placed between two layers of shredded residential-type solid waste; only shredded solid waste was placed in the other cell. To insure that the solid waste added to each of the cells was similiar in composition, the wastes were mixed and then loaded into the cells. A total of 5.5kg (3.9kg dry weight) of solid waste was placed and compacted into each cell.

TABLE 3. Analytical Methods and Instrumentation

Parameter	Method
pH	Standard Methods*; Fisher Accumet pH/mV meter, Model 610
Oxidation-Reduction Potential (ORP)	Standard Methods*; Fisher Accumet pH/mV meter, Model 610
Conductivity	Standard Methods*; YSI Conductivity Bridge, Model 31
Total Alkalinity	Standard Methods*
Total Organic Carbon (TOC)	Standard Methods*; Beckman Total Organic Carbon Analyzer, Model 915
5-Day Biochemical Oxygen Demand (BOD_5)	Standard Methods*
Chemical Oxygen Demand (COD)	Standard Methods*
Volatile Fatty Acids	Direct aqueous injection; Hewlett Packard GC 5710A, packed column - 2 m x 2 mm I.D., Carbopack B 60-80 mesh, modified with 1% carbowax 20 M and 1.5% phosphoric acid
Sulfides	Orion silver/sulfide electrode, Model 94-16 with Fisher Accumet pH/mV meter, Model 610
Metals	Standard Methods*; Perkin Elmer Atomic Absorption Spectrophotometer, Model 303
Carbon, Hydrogen and Nitrogen	Standard Methods*; F&M Scientific Corp. Carbon-Nitrogen-Hydrogen Analyzer, Model 185
Gas Composition	Standard Methods*; Fisher Gas Partitioner

*Standard Methods for the Examination of Water and Wastewater, 15th Ed., APHA, AWWA, WPCF (1981)

To expedite leachate generation, both cells were brought to apparent field capacity by the initial addition of 10 liters of distilled water. This water was added to the cells in small increments as the solid waste was placed and compacted in the cells to maximize uptake of moisture by the solid waste and minimize short-circuiting. Subsequent to the initial addition of water, the cells were sealed to prevent the further entry of air into the cells.

Operational and Sampling Procedures. Since the purpose of these tests was to determine if formaldehyde in the leachate was attributable only to foam or also to other constituents of the solid waste, moisture addition to these cells was provided to insure sufficient volumes of leachate would be generated for formaldehyde determination at periodic intervals. To document that the environmental conditions within each of the cells remained relatively similiar and were representative of actual leaching conditions, additional analyses were performed on selected samples (e.g., pH, COD, TOC, BOD, Conductivity and Alkalinity).

Leaching and Percolation Tests. At the beginning of the research project, leachability and percolation tests were conducted to determine if formaldehyde could be extracted from the foam by immersion of the foam in distilled water and 1% acetic acid solutions (adopted to simulate conditions characteristic of landfill leachates during acid fermentation), and if formaldehyde could be leached from the foam by the percolation of water through the foam, respectively. These tests, which were discussed in detail in the Interim Progress Report,[10] were considered inconclusive since the analytical method used for formaldehyde analysis at that time (i.e., chromotropic acid method) was subject to interferences

from other constituents present in the foam and not considered reliable.

Digestibility Studies

Construction and Preparation of Laboratory-Scale Digestors. To provide an opportunity to separately determine the degradability of formaldehyde present in the leachate from the simulated landfill cells containing SaniFoam by anaerobic processes, as well as possible inhibition to the methanogenic degradation of biodegradable organics present in the leachate due to the constituents contributed by the foam, two batch digestors (2-liter capacity) with necessary appurtenances for substrate addition, sludge removal and gas production monitoring were constructed. Two liters of fresh digested sludge obtained from Clayton Wastewater Treatment Plant, Atlanta, Georgia were placed in each digestor. The digestors were then sealed to the atmosphere and allowed to begin operation according to the following operational and sampling procedure.

Operational and Sampling Procedures. One digestor was used to determine the quantity of gas attributable only to the degradation of biodegradable organic matter already present in the sludge. No subsequent addition of any substrate (leachate) was made to this digestor during the study. The other digestor received daily additions of leachate that had been previously collected from the single-pass cell as a sole source of substrate. Following an initial acclimatization period during which increasing volumes of leachate were added to the digestor corresponding to equal volumes of sludge being removed, leachate addition and sludge removal was maintained constant at 100 ml/day for the duration of the study. In addition, the volumes of gas generated by both digestors were recorded on a daily basis.

Once steady-state conditions with respect to leachate addition

and gas production were attained, supernatant samples were collected at periodic intervals from the digestor receiving leachate as a substrate. These samples, as well as the leachate added to the digestor, were analyzed for pH, COD, TOC, BOD, alkalinity and formaldehyde. Samples of gases generated by the digestors were also collected and analyzed at periodic intervals, primarily for CO_2 and CH_4.

PRESENTATION AND DISCUSSION OF RESULTS

Determination and Quantification of Formaldehyde in Leachates

As previously discussed, analytical method development for the determination and quantification of formaldehyde in leachates was focused on the derivatization of 2,4-dinitrophenylhydrazine (DNP) with formaldehyde to form 2,4-dinitrophenylhydrazone (DNPH) since this technique had been successfully used by several investigators for the determination of trace amounts of aldehydes.[7-9] However, to insure that this technique was a viable method for determination of formaldehyde in leachate and would provide accurate and reproducible results, method validation, reproducibility and recovery studies were performed.

Method Validation Studies. To verify the formation, extraction and analysis of the DNPH derivative, DNP reagent was added to 500 ppb formaldehyde standard solutions prepared in "organic free" water and allowed to react at 45°C for two hours. The derivative was then extracted with methylene chloride, concentrated and then analyzed by glass capillary column GC. Further verification of the DNPH formation was provided by GC-MS analysis. The reconstructed ion chromatogram (RIC) and the mass spectrum of the DNPH are shown in Figures 5 and 6, respectively.

Following this initial success with standard aqueous solutions, the analytical procedure was applied to leachate samples. Results of these tests revealed that DNPH could also be formed, extracted and concentrated from the leachate samples under investigation. Verification of the DNPH derivative was made by GC-MS analysis (Figures 7 and 8).

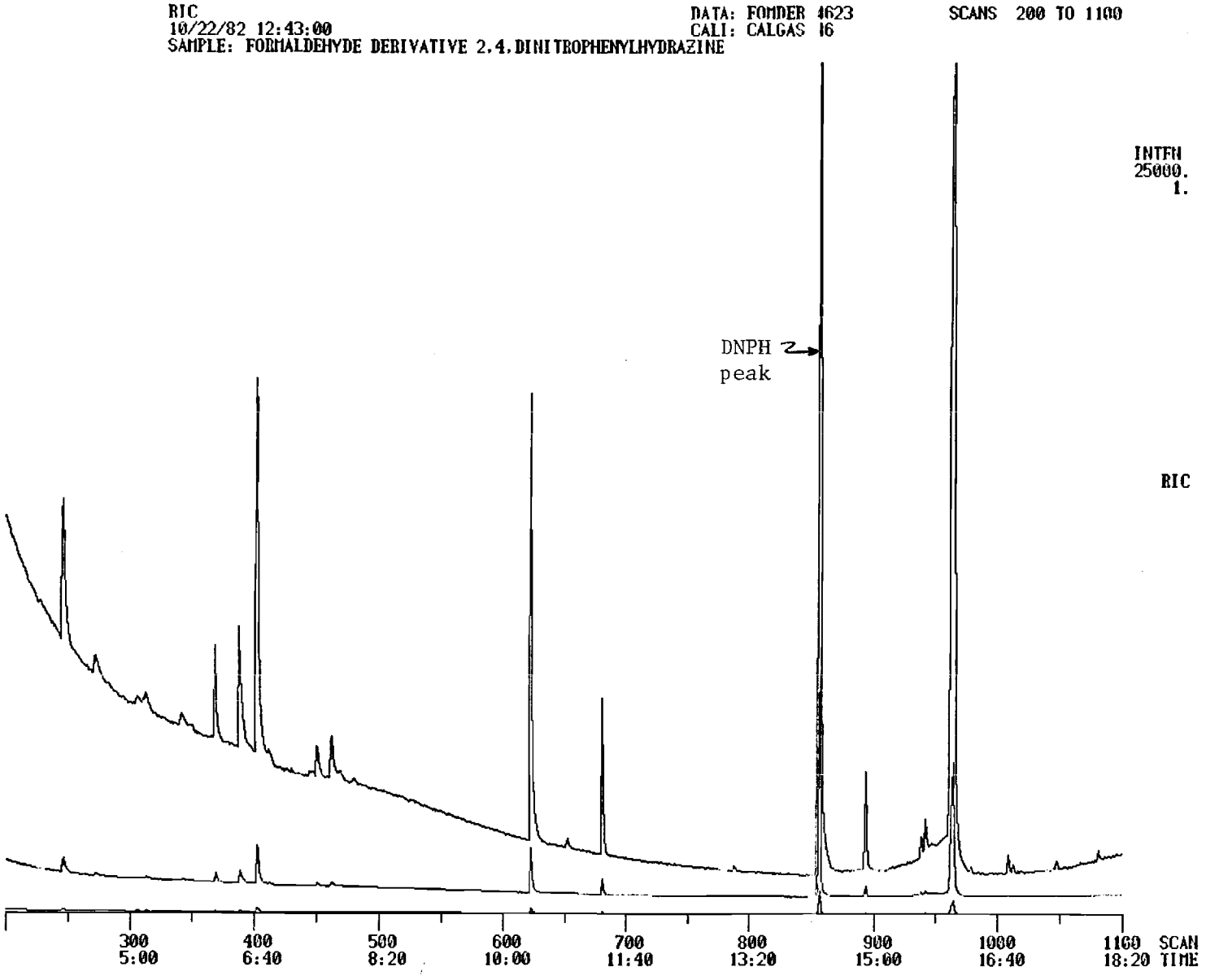


Figure 5. Reconstructed Ion Chromatogram of 2,4-Dinitrophenylhydrazone (DNPH) Derivative

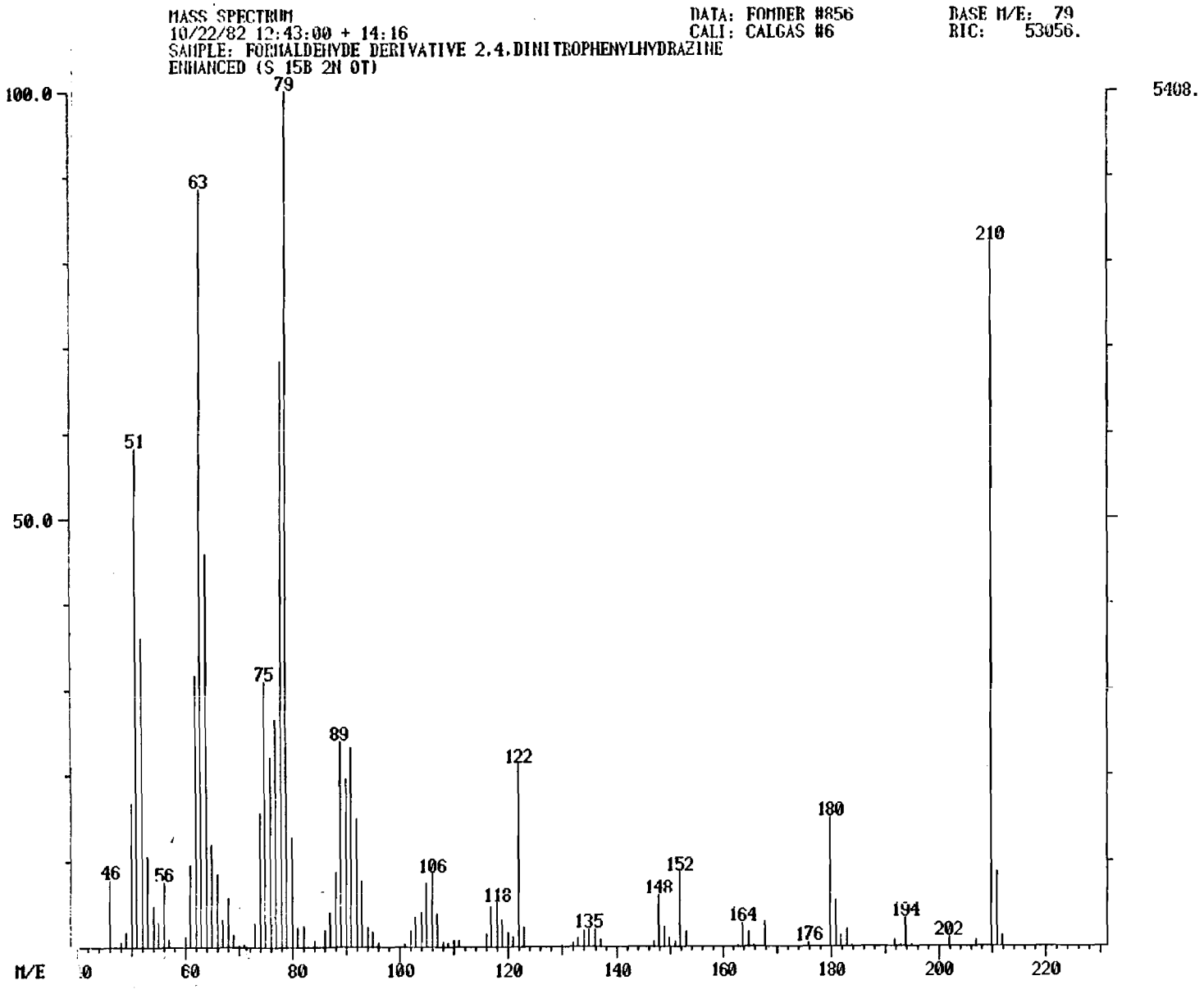


Figure 6. Mass Spectrum of 2,4-Dinitrophenylhydrazone (DNPH)

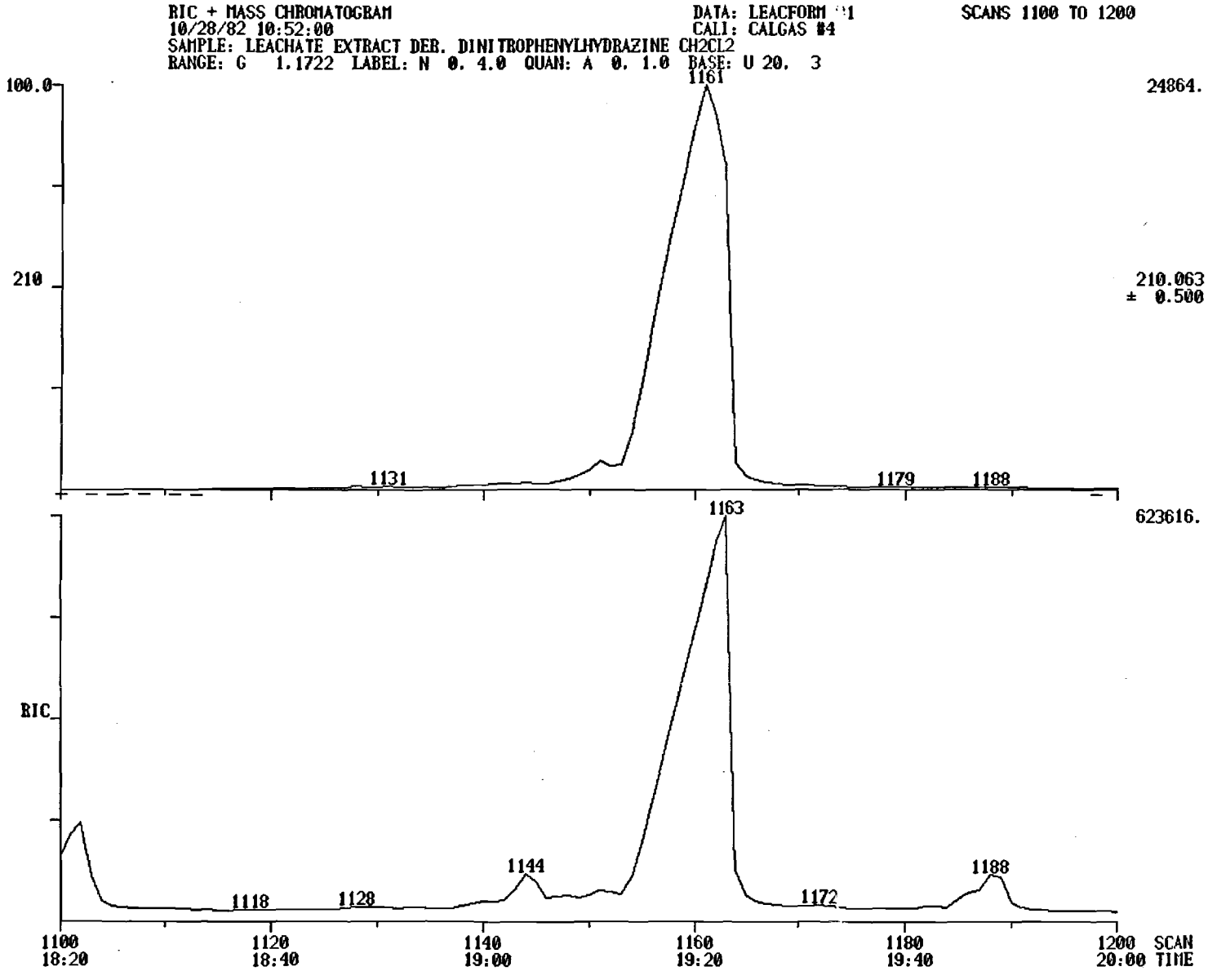


Figure 7. Selected Ion Plot of 2,4-Dinitrophenylhydrazone (DNPH) Extracted from Leachate

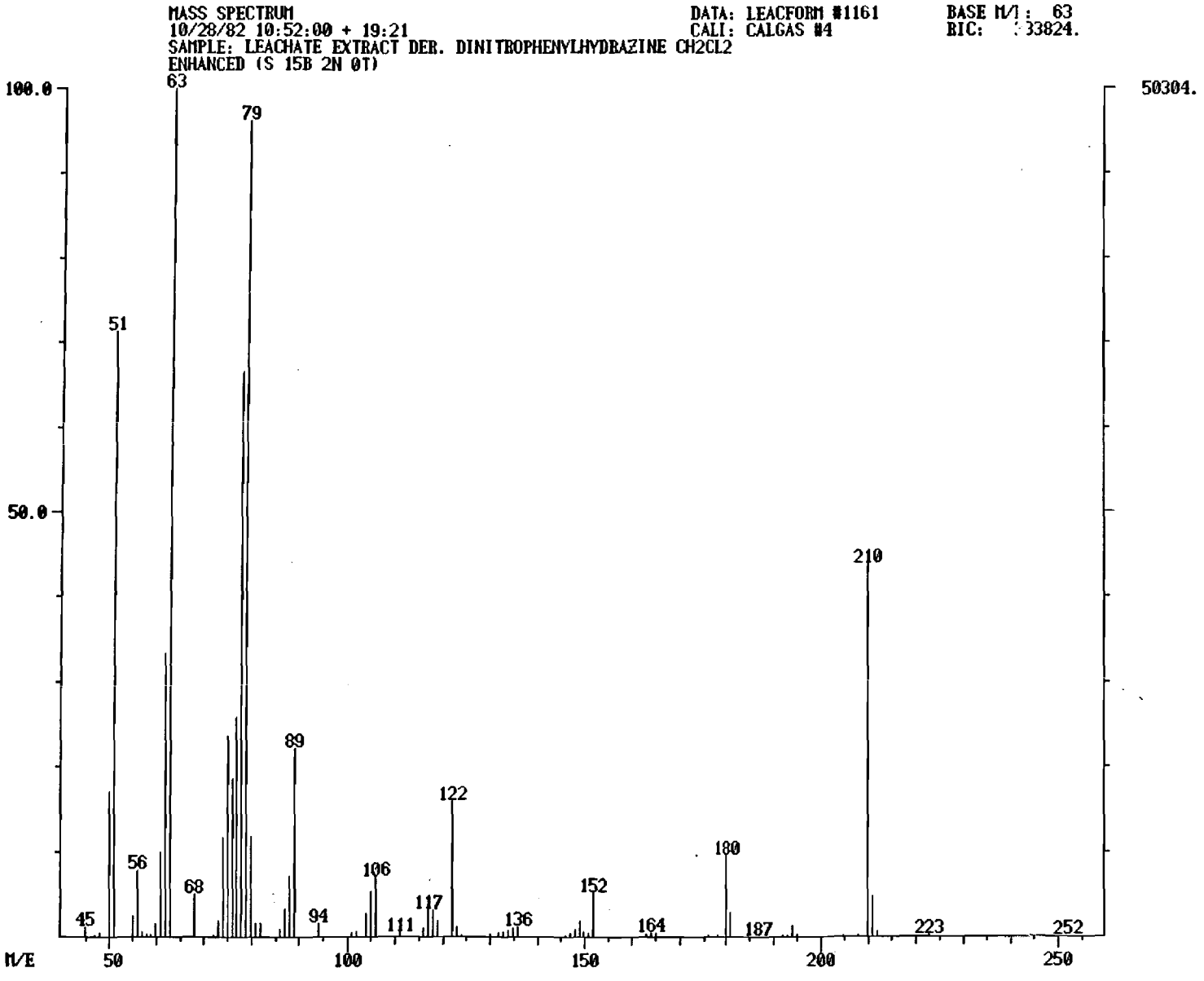


Figure 3. Mass Spectrum of 2,4-Dinitrophenylhydrazone (DNPH) Extracted from Leachate

To insure that the glass capillary column (30m x 0.3mm I.D. SE-54) used for the quantification of DNPH allowed the separation of all dinitrophenylhydrazone derivatives of the C_1-C_4 aldehyde homologs, analysis using "organic-free" water spiked with acetaldehyde, propionaldehyde, and n-butryraldehyde were performed. These results indicated that good separation of all the derivatives was attained.

Upon verification of the formation, extraction and analysis of the DNPH derivative, "blank" determinations were performed with the "organic free" water used in these analyses, as well as the distilled water that was added to the single-pass and recycle simulated landfill cells, to ensure that no formaldehyde was initially present in these aqueous samples or introduced during sample manipulation. Results of these analyses indicated absence of DNPH formation and it was, therefore, concluded that formaldehyde was not initially present.

Method Reproducibility. The reproducibility of the analytical procedure was initially determined by the analysis of distilled water samples spiked with formaldehyde. The results of these analyses are presented in Table 4 and indicated that acceptable reproducibility could be achieved when an internal standard was used for the GC analysis.

Table 4. Reproducibility of Results for the Derivatization of 2,4-dinitrophenylhydrazone (DNPH) in Distilled Water

Sample Identification*	Amount of DNPH measured, nanograms**	Mean	Standard Deviation	Coefficient of Variation
W-1	86.3			
W-2	99.4	93.5	6.0	6.4%
W-3	94.7			

*Samples consisted of distilled water spiked with formaldehyde and subsequently divided into 3 aliquots.

**Internal Standard: Perylene-d_{12}

Tests conducted to determine the reproducibility of the method for leachate samples during the early stages of method development indicated a high variance in results. This was primarily attributed to the fact that external standards were used for the GC analysis since the internal standard initially selected had a retention time that coincided with that of other co-extracted compounds present in the leachate. Another cause of high variance was attributed to the formation of thick emulsions when extracting leachate samples with methylene chloride.

To improve reproducibility for leachate analysis, internal standards whose retention times did not coincide with co-extracted compounds were selected and leachate samples were diluted with distilled water to reduce the formation of emulsions during solvent extraction. Results of leachate sample analysis subsequent to these procedural modifications are presented in Table 5 and indicate that good reproducibility was achieved.

Table 5. Reproducibility of Results for the Derivatization of 2,4-dinitrophenylhydrazone (DNPH) in Leachate Samples

Sample Identification*	Amount of DNPH measured, nanograms**	Mean	Standard Deviation	Coefficient of Variation
L-1	125.4			
L-2	128.4	132.2	7.5	5.7%
L-3	142.7			

*Samples consisted of leachate sample from the single-pass cell diluted 50% with distilled water and subsequently divided into 3 aliquots.

**Internal Standard: Perylene-d_{12}

Recovery Studies. Recovery studies were conducted to determine the amount of DNPH that could be recovered from the aqueous sample by solvent extraction and concentration following derivative formation. To perform these studies, leachate samples were divided into two fractions and derivatization of the formaldehyde present in both fractions with an excess of 2,4-dinitrophenylhydrazine under acidic conditions was accomplished. One fraction was then spiked with a known amount of DNPH (45.0 ng) prior to solvent extraction and sample concentration. Results of these studies are summarized in Table 6. Based on these results, the mean recovery of DNPH from leachate samples was found to be 55.3 ± 3.8%. This level of recovery was considered satisfactory based on the fact that recoveries of micro-amounts of organic priority pollutants in environmental samples of similar matrix complexity (i.e., municipal raw sewage and sludge) were found to range between 30 and 100%[11].

Table 6. Results from Recovery Studies of DNPH from Leachate Samples

Sample Identification	Amount of DNPH Measured, nanograms	Mean	Standard Deviation	Coefficient of Variation
Leachate Samples				
L-1	125.4			
L-2	128.4	131.1	6.1	4.6%
L-3	139.5			
Leachate Samples Spiked with 45.0 nanograms DNPH				
LS-4	150.7			
LS-5	161.5	156.0	4.4	2.8%
LS-6	155.9			

Landfill Simulation Studies

Data from the landfill simulation studies are presented in Tables 7 through 24 and Figures 9 through 39. These data record the results of environmental conditions during the study period as well as solid waste characteristics and analyses on leachate and gas samples. The relation of the time scale used in presentation of data, i.e., time since leachate generation began, to the actual sampling date is presented in Table 7.

Solid Waste Characteristics. The original solid waste characteristics are included in Table 8. These analyses were intended to provide comparative information on the nature of the solid waste within each cell initially and at the termination of the study. Since both landfill simulation cells are still operational, these latter data are not yet available.

Environmental Conditions. Ambient and simulated landfill cell temperatures are presented in Table 9 and Figure 9. The landfill cell temperatures varied with the ambient temperature of the room where the cells were located. The temperatures within both cells were very similiar on most occasions during the first 350 days of the study. Hence, the effect of temperature differences on biological activity between the cells during this time period was considered minimal. The relatively higher temperatures measured in the recycle cell between Days 353 and 430 tended to correspond with the period during which an increase in microbial activity (as indicated by increased gas production) was observed.

Leachate Characterization. COD, TOC and BOD_5 analyses of the leachate were used to reflect pollutional impact derived from the organic matter in the solid waste. The initial high concentrations of

Table 7. Sampling Date and Corresponding Day as "Time Since Leachate Generation Began"

Sampling Date	Time Since Leachate Generation Began, days	Sampling Date	Time Since Leachate Generation Began, days
07/17/82	6	03/11/83	243
07/23/82	12	03/25/83	257
07/30/82	19	04/08/83	271
08/07/82	27	04/22/83	285
08/14/82	34	05/14/83	307
08/23/82	43	06/09/83	333
08/31/82	51	06/27/83	351
09/06/82	57	07/05/83	359
09/13/82	64	07/17/83	369
09/21/82	71	07/27/83	381
09/27/82	77	08/03/83	388
10/04/82	84	08/12/83	397
10/11/82	91	08/19/83	404
10/18/82	98	08/26/83	411
10/26/82	106	09/02/83	418
11/01/82	111	09/09/83	425
11/07/82	117	09/22/83	438
11/15/82	125	09/30/83	446
11/22/82	132	10/11/83	457
11/29/82	141	10/18/83	464
12/07/82	149	10/24/83	470
12/14/82	156	11/02/83	479
12/28/82	170	11/08/83	485
01/12/83	185	11/11/83	488
01/25/83	198	11/18/83	495
02/08/83	212	11/22/83	499
02/25/83	229	11/29/83	506

COD, TOC and BOD_5 (Tables 10 and 11 and Figures 10-12) were the result of the solubilization and extraction of organics present in the solid waste. The decrease that was observed in these parameters during the first 60 to 80 days was attributable to the dilution effect of moisture additions during this time period (See Table 2 and Figure 4) in the recycle cell and the washout and removal of these constituents from the single-pass cell. The concentrations of these parameters measured subsequent to this period and to about Day 400 were indicative of a prolonged period of acid fermentation and that phase of landfill stabilization.[4]

Table 8. Characterization of Solid Waste Added to Simulated Landfill Cells

Parameter	Solid Waste Characteristics	
	Single-Pass Cell	Recyle Cell
Amount of solid waste added:		
- as placed, kg	60 (132.3)*	60 (132.3)*
- dry weight, kg	39 (86.0)*	39 (86.0)*
Moisture Content	35	35
Density, kg/m^3	373.5 (629.6)**	372(627.5)**
Volatile Solids, %	73.4	74.2
Amount of foam in cell, % of total solid waste volume	8	8
Carbon (dry weight), %	43.8	43.8
Hydrogen (dry weight), %	5.8	5.8
Nitrogen (dry weight), %	6.2	6.2

*lb
**lb/yd^3

The higher concentrations of these parameters in the leachate from the recycle cell as compared with the single-pass cell were attributable to the different removal mechanisms in each cell. In the recycle cell, daily recycle of leachate provided a continuing exposure of the waste

Table 9. Ambient and Internal Cell Temperatures

Sample Day	Temperature, °C		
	Recycle Cell	Single-Pass Cell	Ambient
6	31.0	30.2	29.5
12	29.0	28.2	29.5
19	31.0	30.8	31.5
27	30.6	30.4	29.0
34	28.2	27.8	28.0
43	28.0	27.3	28.0
51	28.2	28.2	30.0
58	25.8	25.6	24.5
64	26.4	26.0	25.5
71	26.4	27.0	27.5
77	26.4	26.4	26.5
84	25.8	26.0	27.0
91	28.2	27.0	29.0
98	24.0	23.6	25.0
106	26.8	26.4	26.0
111	25.8	24.6	26.0
117	27.2	24.8	25.0
125	26.8	26.0	20.0
132	25.4	24.6	24.2
141	28.8	27.4	27.5
149	29.5	27.3	26.0
156	23.4	22.8	22.5
170	30.3	28.5	30.0
185	28.9	27.1	26.0
198	25.0	24.0	24.0
212	25.0	23.5	25.0
229	28.6	27.1	27.5
243	27.2	26.0	25.0
257	26.8	25.6	27.0
271	30.3	28.8	28.5
285	24.0	23.0	26.3
307	26.8	26.4	27.0
333	25.0	26.8	27.5
351	31.0	28.8	31.0
359	29.5	27.7	27.5
369	32.4	29.2	31.5
381	32.4	29.5	28.5
388	28.9	27.5	28.0
397	32.4	28.8	28.5
404	31.0	28.4	28.0

(Continued)

Table 9. (Continued)

Sample Day	Temperature, °C		
	Recycle Cell	Single-Pass Cell	Ambient
411	31.7	28.4	27.5
418	28.9	27.3	24.0
425	29.5	27.7	28.0
438	28.2	27.7	28.0
442	28.9	28.4	28.5
446	29.5	28.2	28.5
457	27.2	26.5	25.0
464	26.8	25.6	27.5
470	26.6	25.1	25.5
479	31.7	28.2	28.8
485	30.3	27.9	29.5
493	30.3	29.2	28.5

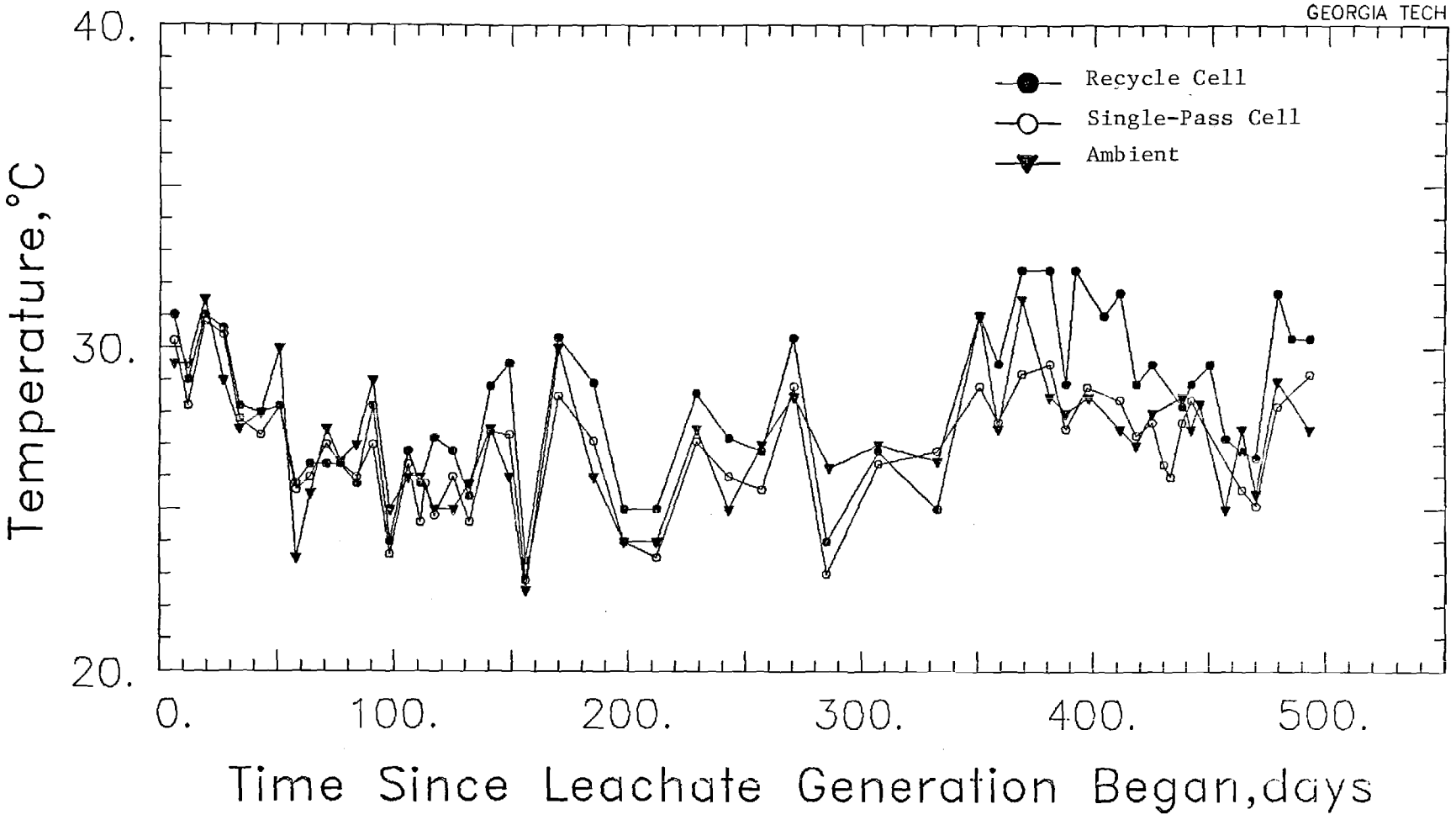


Figure 9. Ambient and Simulated Landfill Cell Temperatures

Table 10. pH, ORP, Conductivity, Alkalinity, COD, TOC, BOD_5 and Sulfide Concentrations in Leachate Samples from the Recycle Cell

Sampling Day	pH	ORP, mV E_c	Conductivity, μmhos/cm	Alkalinity, mg/l as $CaCO_3$*	COD, mg/l	TOC, mg/l	BOD_5, mg/l	Sulfide, mg/l
6	4.23	-40	24,000	8,900	58,000	24,000	-	-
12	4.27	-112	24,000	11,800	96,000	28,400	4,500	<0.1
19	5.26	-70	15,000	8,000	40,000	10,700	35,000	0.5
27	5.12	-65	15,000	8,700	37,500	11,100	19,500	<0.1
34	5.05	-25	14,000	8,300	34,000	11,900	25,800	<0.1
43	4.98	-001	14,000	8,000	26,900	11,800	23,000	<0.1
51	5.21	-10	14,000	7,800	29,000	12,000	18,000	<0.1
57	5.06	+40	12,120	7,000	29,100	10,300	18,600	<0.1
64	4.97	+18	11,300	7,000	28,500	9,700	15,000	<0.1
71	4.97	+24	10,700	6,300	27,900	10,200	13,800	<0.1
77	5.00	-02	13,000	6,500	27,300	9,800	19,000	<0.1
84	5.02	-04	12,800	6,800	29,600	9,400	19,800	-
91	4.98	-31	12,300	6,800	29,800	8,700	11,600	<0.1
98	4.97	-20	11,700	6,700	28,900	10,500	17,400	-
106	5.02	-20	12,600	6,700	31,200	8,800	15,700	0.3
111	5.02	-15	12,200	6,250	29,600	8,700	-	-
117	5.02	-15	11,800	6,750	29,800	9,400	20,100	<0.1
125	4.98	-15	12,800	6,500	31,700	9,800	-	<0.1
132	5.09	-05	13,800	6,250	30,300	13,300	16,100	<0.1
141	5.03	-13	13,500	6,700	29,700	14,000	15,500	-
149	5.05	-26	13,200	6,650	29,000	-	12,300	-
156	5.03	-30	13,500	6,630	30,200	11,700	17,700	-
170	5.05	-31	14,500	6,500	26,800	11,300	-	-
185	5.04	-40	14,200	6,430	26,900	12,200	-	-
198	5.05	-45	13,000	5,500	29,700	9,800	-	-
212	5.05	-41	13,500	7,000	29,800	9,200	-	<0.1
229	5.05	-45	13,400	7,430	30,700	-	-	-
243	5.05	-40	13,800	7,620	32,600	9,300	-	-
257	5.06	-34	13,600	7,880	27,800	10,080	-	<0.1
271	5.10	-36	13,700	8,175	31,290	10,400	29,500	-
285	5.13	-57	13,800	8,210	33,400	10,200	24,000	-
307	5.17	-50	14,000	8,250	31,800	-	26,400	<0.1

(Continued)

Table 10. (Continued)

Sampling Day	pH	ORP, mV E_c	Conductivity, μmhos/cm	Alkalinity, mg/l as $CaCO_3$*	COD, mg/l	TOC, mg/l	BOD_5, mg/l	Sulfide, mg/l
333	5.15	-65	13,700	8,480	33,800	11,300	-	-
351	5.12	-80	13,400	9,000	33,100	-	17,100	<0.1
359	5.18	-65	13,500	8.950	33,900	11,500	-	-
369	5.11	-58	13,400	8,750	-	10,870	-	-
381	5.13	-60	13,200	9,000	33,500	10,750	-	-
388	5.19	-55	13,000	8,200	34,400	10,420	-	<0.1
397	5.19	-60	12,800	7,850	27,400	9,536	19,800	-
404	5.15	-47	12,400	-	25,800	9,470	21,600	-
411	5.17	-52	11,900	-	24,700	9,400	21,000	-
418	5.19	-60	11,700	-	23,500	9,350	-	-
425	5.19	-59	10,010	-	20,850	-	13,200	<0.1
438	5.15	-57	8,200	4,350	16,210	6,800	10,470	-
446	5.15	-63	-	-	15,030	7,000	9,063	-
457	5.17	-65	-	-	15,100	6,600	8,125	-
464	5.19	-	6,000	3,925	-	-	-	-
470	5.53	-84	4,900	2,650	9,540	2,390	4,450	-
479	6.03	-114	-	-	5,300	2,100	2,600	<0.1
485	6.53	-150	4,300	-	-	-	-	-
488	6.46	-153	-	2,100	3,150	2,050	1,360	-
495	-	-	-	-	2,890	1,185	775	-
499	6.71	-203	-	-	-	-	-	-
506	6.83	-203	-	2,050	2,445	830	450	0.12

*Determined by titration to pH 3.5.

Table 11. pH, ORP, Conductivity, Alkalinity, COD, TOC, BOD_5 and Sulfide Concentrations in Leachate Samples from Single-Pass Cell

Sampling Day	pH	ORP, mV E_c	Conductivity, µmhos/cm	Alkalinity, mg/l as $CaCO_3$*	COD, mg/l	TOC, mg/l	BOD_5, mg/l	Sulfide, mg/l
6	4.51	-100	22,000	10,400	77,000	26,100	-	-
12	6.47	-300	23,000	17,800	85,000	22,500	11,300	<0.1
19	6.25	-280	22,000	17,700	80,000	25,000	50,000	0.3
27	5.92	-125	22,000	15,400	72,000	21,800	36,000	0.3
34	5.58	-70	20,000	13,800	62,400	19,800	34,000	0.2
43	5.28	-33	17,000	11,800	46,500	17,200	40,000	0.1
51	5.35	-150	14,000	9,500	41,800	15,400	24,600	0.1
57	5.05	+42	11,500	6,600	29,800	11,500	17,000	<0.1
64	4.90	+15	10,000	6,300	30,500	9,700	12,000	<0.1
71	4.81	+17	8,500	5,100	27,800	9,800	16,500	<0.1
77	4.81	+08	9,200	5,100	24,700	8,800	15,300	<0.1
84	4.84	+08	9,100	4,900	21,000	8,500	14,400	-
91	4.78	-49	8,800	4,600	20,700	7,700	12,500	<0.1
98	4.81	-	8,500	4,800	20,800	8,100	14,800	-
106	4.87	0	8,000	5,000	21,600	8,700	11,600	-
111	4.90	-20	9,200	5,000	22,900	9,000	-	-
117	4.83	-17	8,500	5,000	19,700	7,900	14,500	<0.1
125	4.80	-15	8,000	4,900	22,500	7,400	-	<0.1
132	4.90	-15	10,400	4,750	17,200	8,400	7,500	<0.1
141	4.87	-15	9,800	4,600	20,300	8,700	11,800	-
149	4.90	-40	9,800	5,200	22,000	-	9,500	-
156	4,88	-30	9,200	5,200	21,500	9,400	3,700	-
170	4.88	-39	11,000	5,300	18,800	9,800	-	<0.1
185	4.95	-50	10,800	5,430	20,600	9,500	-	-
198	4.97	-58	11,000	4,600	23,600	7,000	-	-
212	5.00	-60	9,500	4,600	18,300	6,800	-	-
229	5.01	-51	9,600	6,500	22,700	-	-	-
243	5.05	-50	9,400	6,500	21,800	7,100	-	-
257	5.10	-50	9,500	6,630	21,500	6,300	-	<0.1
271	5.15	-66	9,400	6,500	20,000	7,600	16,400	-

(Continued)

Table 11. (Continued)

Sampling Day	pH	ORP, mV E_c	Conductivity, μmhos/cm	Alkalinity, mg/l as $CaCO_3$*	COD, mg/l	TOC, mg/l	BOD_5, mg/l	Sulfide, mg/l
285	5.22	-85	9,400	6,550	21,500	8,000	15,200	-
307	5.25	-85	9,400	6,850	20,000	-	17,000	<0.1
333	5.18	-87	9,300	7,030	22,200	8,100	-	-
351	5.10	-70	9,300	7,150	23,100	-	14,500	<0.1
359	5.19	-75	9,200	6,830	22,000	8,200	-	-
369	5.11	-72	8,900	6,250	-	7,800	-	-
381	5.11	-70	8,600	5,950	19,100	8,100	-	-
388	5.19	-68	8,400	5,300	18,100	7,200	-	-
397	5.13	-70	8,200	5,400	17,700	8,200	11,600	-
404	5.15	-58	8,400	-	17,600	7,800	15,900	-
411	5.15	-52	8,200	-	17,800	8,600	15,800	-
418	5.17	-49	8,000	-	18,900	6,900	-	-
425	5.19	-56	7,500	5,350	18,600	-	12,500	<0.1
438	5.18	-53	7,600	5,080	19,240	7,500	11,750	-
446	5.17	-54	-	-	18,610	8,300	12,190	-
457	5.18	-48	-	-	18,800	7,250	10,885	-
464	5.15	-	7,100	5,150	-	-	-	-
470	5.19	-45	6,000	5,500	19,170	5,400	11,500	-
479	5.18	-33	-	-	18,250	7,300	13,300	<0.1
485	5.17	-56	5,600	-	-	-	-	-
488	5.20	-53	-	5,200	18,900	-	12,800	-
495	-	-	-	-	17,300	7,500	10,000	-
499	5.15	-45	5,300	-	-	-	-	-
506	5.13	-53	-	4,825	18,000	6,300	8,400	<0.1

*Determined by Titration to pH 3.5.

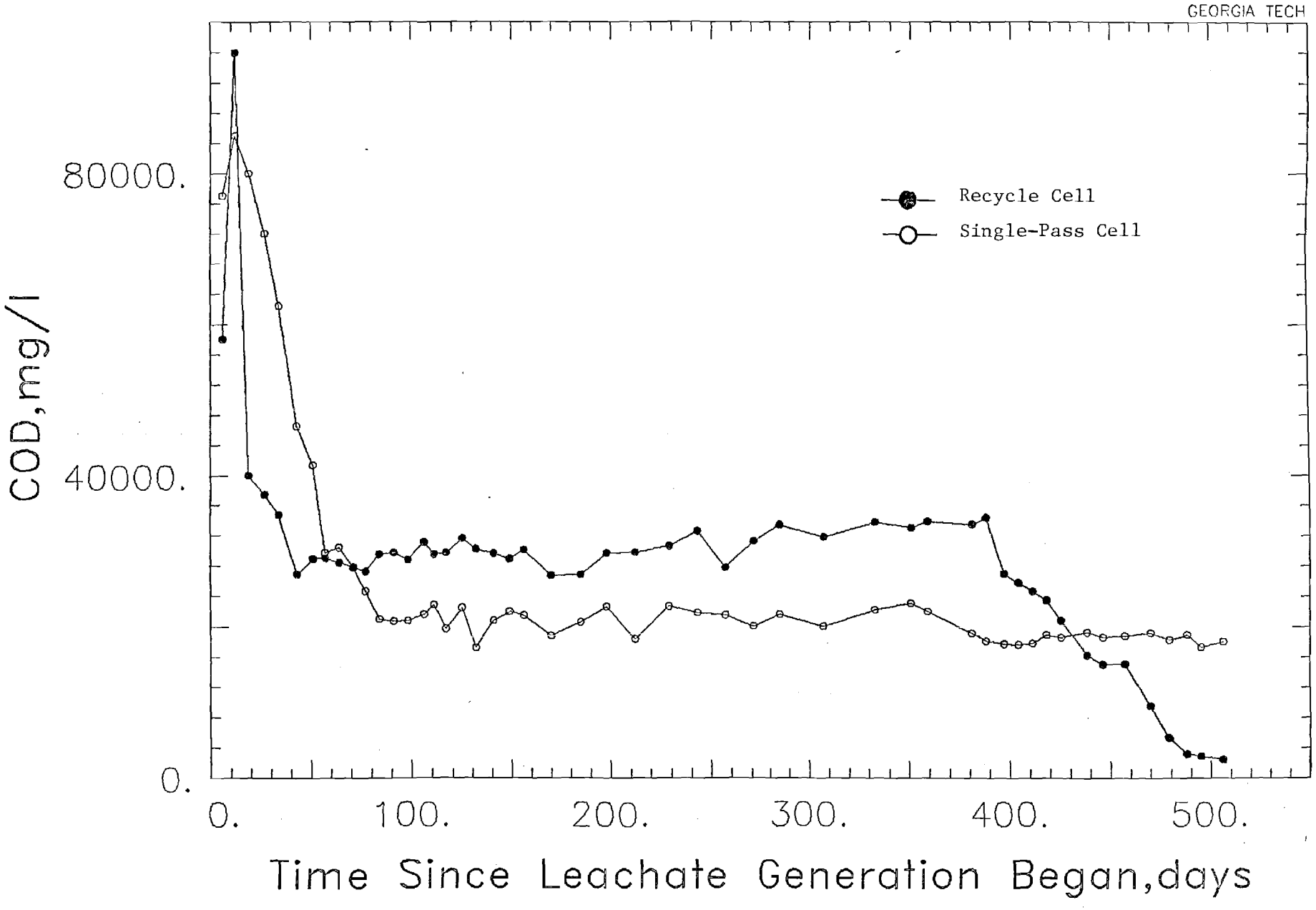


Figure 10. Chemical Oxygen Demand of Leachate

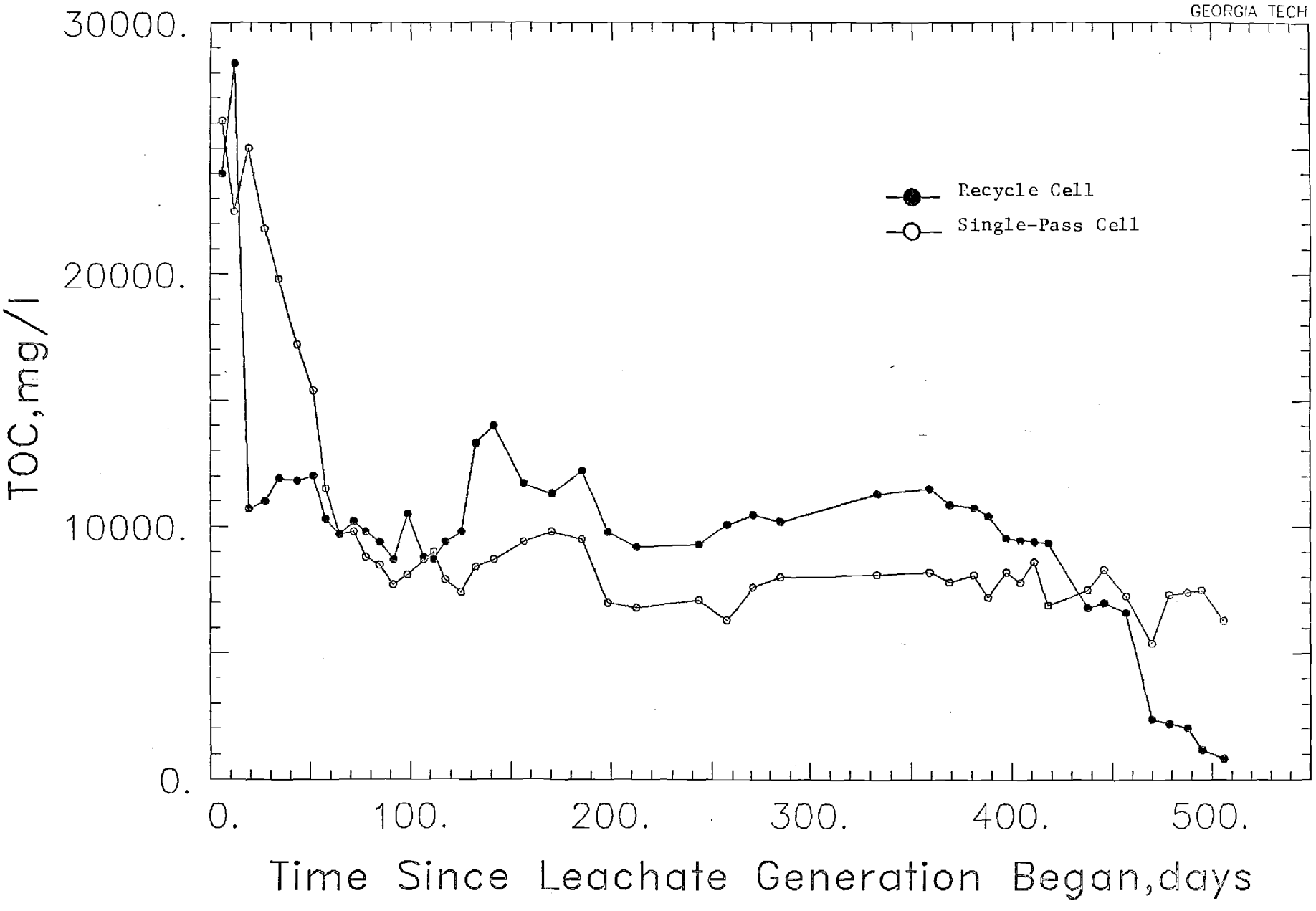


Figure 11. Total Organic Carbon Content of Leachate

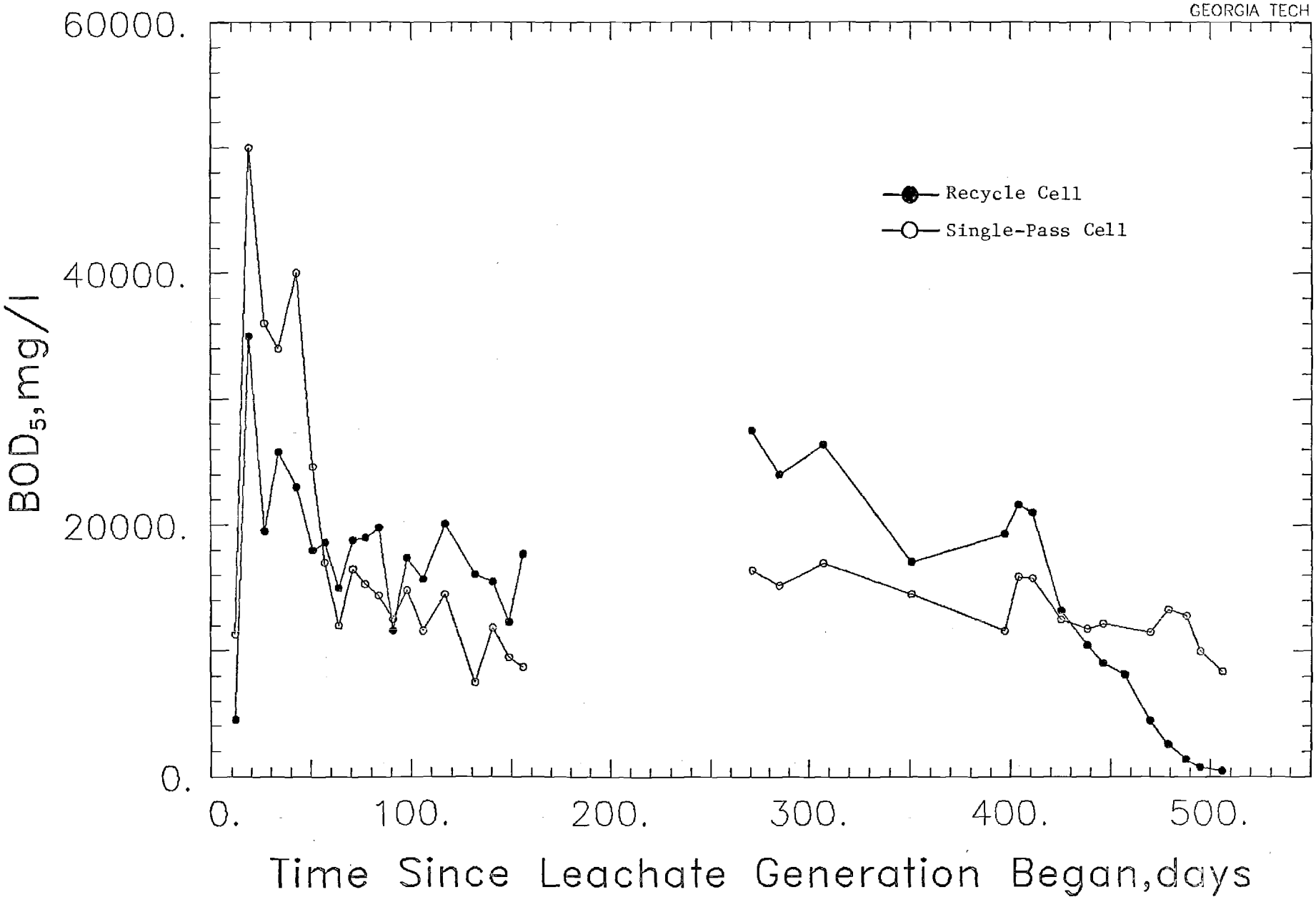


Figure 12. Five-day Biochemical Oxygen Demand of Leachate

and internal microbial populations to the leachate and the nutrients contained in the leachate. This encouraged initial extraction of organics in a more homogeneous manner and eventually enhanced the overall conversion of these constituents to end products (CO_2 and CH_4). Because most of the leachate so generated was contained within the cell, higher concentrations of contaminants accumulated in this cell than in the single-pass cell where the organics present in the solid waste were routinely washed out by single-pass moisture addition and were, therefore, also less available for microbial utilization. As a result, lower concentrations of organic contaminants were measured in the leachate from the single-pass cell, a lower overall efficiency of organic in situ treatment could be expected, and the potential for pollution would be higher if the leachate was released to the environment.

The rapid declines of COD and TOC observed after Day 390 and of BOD_5 after Day 410 in the recycle cell were considered indicative of accelerated biological stabilization of the more readily available organic constituents in the recycled leachate. This increased transformation was augmented by the addition of seed sludge and the onset of methanogenesis.

Further interpretations of changes in pollutional characteristics of the leachate were also possible. Since biological stabilization during landfill disposal of solid waste depends largely on anaerobic microbial activity, the two-phase process of acid fermentation with the conversion of readily biodegradable organics to short-chain fatty acid intermediates followed by fermentation of these products to CH_4 and CO_2 could also be observed. Accordingly, the initial appearance of

volatile acids in the leachate from both cells and the subsequent utilization of these acids in the recycle cell system (Tables 12 and 13 and Figures 13-15) corresponded to the trends observed for the COD, TOC and BOD_5 analyses. Furthermore, this sequential behavior of acid formation and subsequent methane fermentation in the recycle cell could be contrasted with the continuation of acid formation in the single-pass cell where the opportunity for promoting the development of active methanogenesis was greatly curtailed by the mode of operation.

As could be anticipated, accumulations of volatile acids caused an initial decrease in the pH of both cells (Tables 10 and 11 and Figure 16). Moreover, decreased pH conditions were sustained in the single-pass cell as volatile acid concentrations within the cell remained high and unchanged except for dilution effects. In contrast, a rapid increase in pH toward neutral was observed in the recycle cell as volatile acids were microbially converted and removed.

The alkalinity of the leachate samples served as an indicator of the buffer capacity of the systems. In the presence of high concentrations of volatile acids, the alkalinity of both cells reflected the presence of a buffer system controlled by volatile acids (Tables 10 and 11 and Figure 17). Similarly, the decreased alkalinity in the leachate from the recycle cell corresponded to the conversion and removal of volatile acids and subsequent buffer shift to the domain of the bicarbonate system. This shift was also shown by a more rapid decrease in conductivity in the recycle cell (Tables 10 and 11 and Figure 18), whereas the decreasing trend in conductivity of the single-pass cell was more attributable to the continuing washout of constituents present in this cell.

Table 12. Volatile Fatty Acids Content of Leachate from Recycle Cell

Sampling Day	Acetic Acid, mg/l	Propionic Acid, mg/l	Iso-butyric Acid, mg/l	Butyric Acid, mg/l	Valeric Acid, mg/l	Total, mg/l as Acetic Acid
27	12,700	9,300	1,100	11,500	3,000	30,590
34	13,100	3,100	1,100	12,100	3,000	26,360
64	3,800	4,500	500	2,000	400	9,380
71	7,300	1,100	500	2,100	300	10,140
84	5,250	1,680	370	4,430	930	10,430
91	5,100	1,440	440	3,680	900	9,600
98	6,170	1,630	460	3,890	980	11,030
111	3,820	1,480	380	3,300	750	7,970
117	4,480	950	340	3,370	1,030	8,390
125	4,680	1,120	370	3,400	810	8,640
132	2,990	1,010	470	4,070	1,040	9,210
141	4,030	1,540	1,250	4,640	750	9,720
149	2,630	1,540	500	3,950	1,060	7,520
156	1,420	1,550	540	4,440	950	6,610
170	1,610	810	870	3,960	1,610	6,500
198	2,290	1,350	550	2,650	550	5,870
243	2,410	660	270	1,810	340	4,480
257	3,390	630	500	1,410	290	5,370
271	2,070	680	190	1,430	360	3,830
304	4,380	2,030	680	4,130	1,270	10,050
328	6,780	2,230	670	4,570	1,580	13,100
332	5,090	1,940	690	4,990	1,000	11,050
366	5,620	2,140	970	5,070	1,300	12,230
374	5,100	1,750	810	4,900	1,030	11,070
382	7,970	1,790	750	3,730	600	12,890
395	4,940	1,380	650	3,830	1,020	9,710
405	5,450	2,120	500	2,700	800	9,760
415	5,690	2,830	470	2,440	920	10,500
425	4,850	2,830	310	1,570	780	8,800
431	4,870	2,780	190	1,060	590	8,320
440	3,690	3,620	180	640	560	7,510
449	2,760	4,590	135	375	610	7,185
457	2,200	5,600	75	325	540	7,840
470	800	1,870	35	95	160	2,500
480	925	1,020	25	65	95	1,870
487	650	560	15	90	40	1,200

Table 13. Volatile Fatty Acids Content of Leachate From Single-Pass Cell

Sampling Day	Acetic Acid, mg/l	Propionic Acid, mg/l	Iso-butyric Acid, mg/l	Butyric Acid, mg/l	Valeric Acid, mg/l	Total, mg/l as Acetic Acid
27	10,310	5,000	700	27,800	6,200	37,440
34	7,210	3,400	9,600	16,600	1,500	28,720
64	4,420	2,600	800	3,300	800	9,780
71	4,310	2,300	800	2,700	700	8,950
84	4,450	1,490	500	3,550	940	8,960
91	5,100	1,440	440	3,680	900	9,580
98	5,800	1,340	580	2,680	650	9,500
111	3,820	1,480	380	3,300	750	7,970
117	4,220	920	430	2,280	630	7,170
125	4,680	1,420	370	3,400	570	8,740
132	3,000	860	440	1,690	450	5,400
141	2,250	1,200	700	2,340	530	5,610
149	2,740	1,260	660	2,690	350	6,250
156	2,240	1,270	720	2,960	600	6,120
170	2,200	850	820	2,580	740	5,630
198	2,940	1,210	960	2,030	400	6,180
243	4,800	790	600	440	150	3,850
257	1,860	450	320	890	230	3,190
271	1,220	80	190	580	140	1,830
304	4,210	1,180	880	2,470	620	7,820
328	1,660	320	410	630	240	2,770
332	2,880	700	520	1,470	330	5,000
366	6,540	1,010	990	2,690	560	10,190
374	6,480	990	970	3,400	590	10,600
382	4,500	1,130	1,190	3,580	360	8,880
395	5,680	570	650	2,060	410	8,230
405	5,000	600	675	1,900	330	7,430
415	4,750	660	860	2,360	450	7,740
425	4,800	320	710	2,230	440	7,310
431	4,820	640	650	1,840	390	7,260
440	4,800	620	810	2,730	425	7,930
449	4,650	550	730	2,110	400	7,270
457	7,110	710	730	2,830	400	10,340
470	5,600	800	760	2,200	400	8,500
487	5,830	660	730	2,350	300	8,710

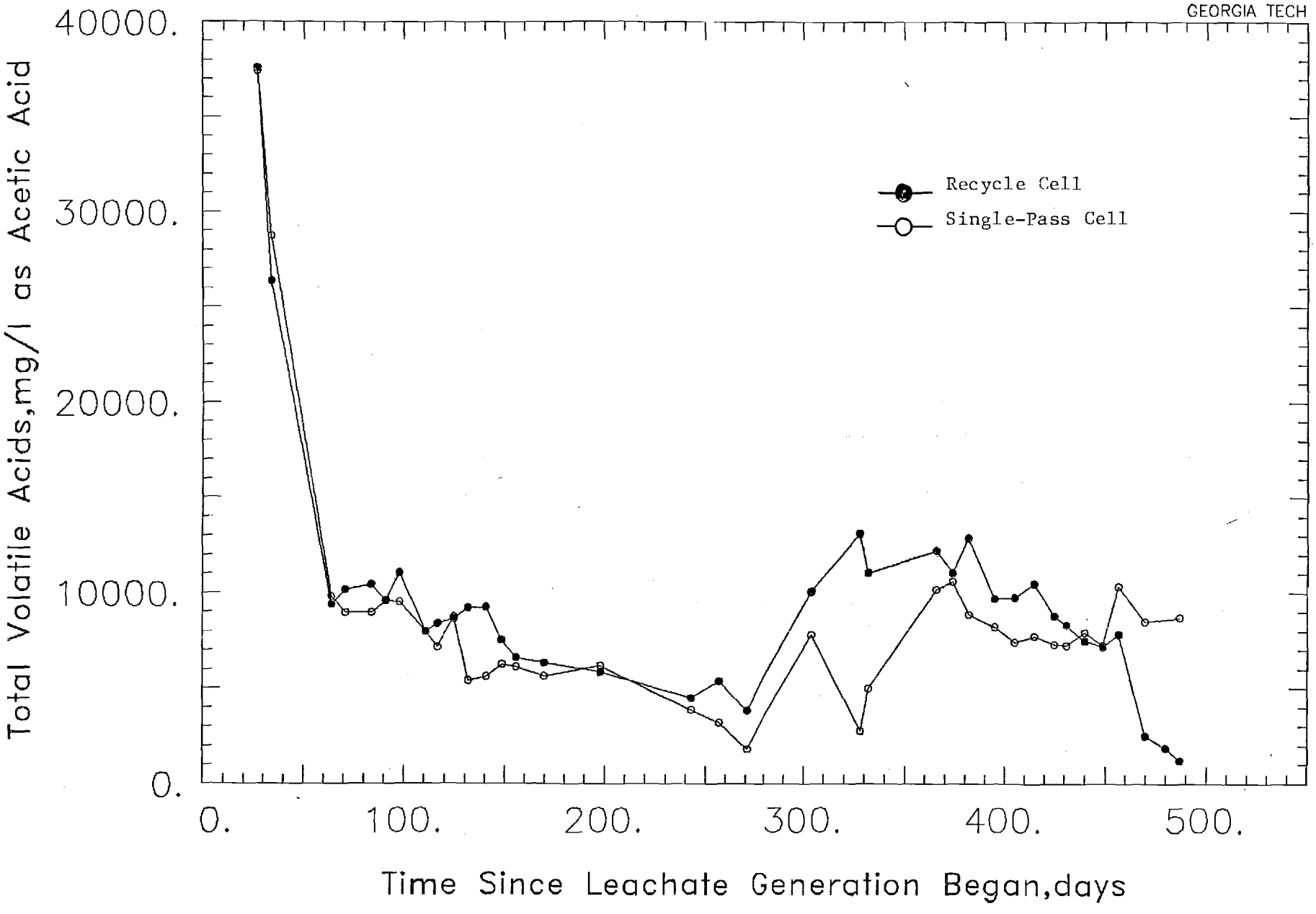


Figure 13. Total Volatile Fatty Acid Content of Leachate

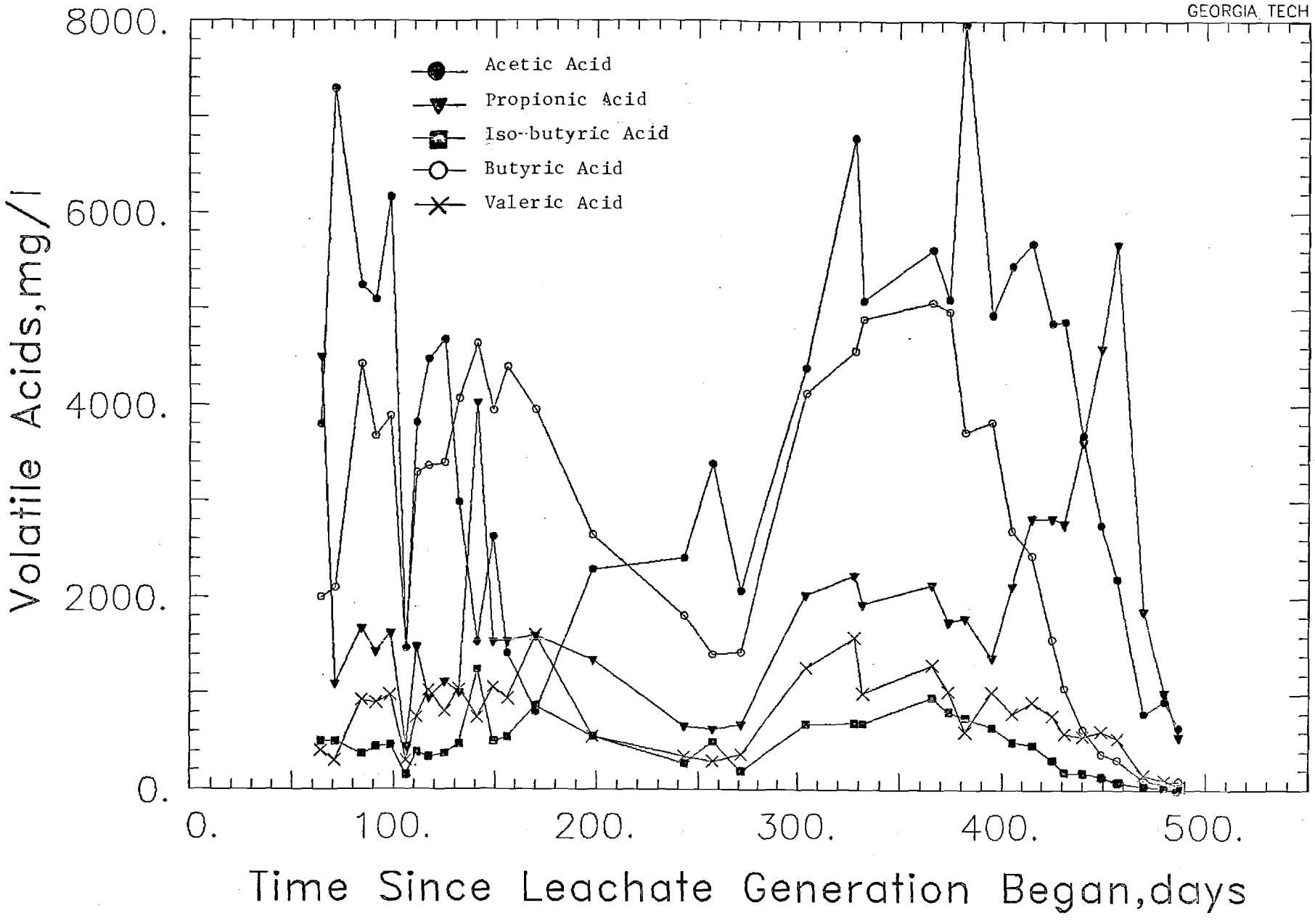


Figure 14. Individual Volatile Fatty Acids Content of Leachate from the Recycle Cell

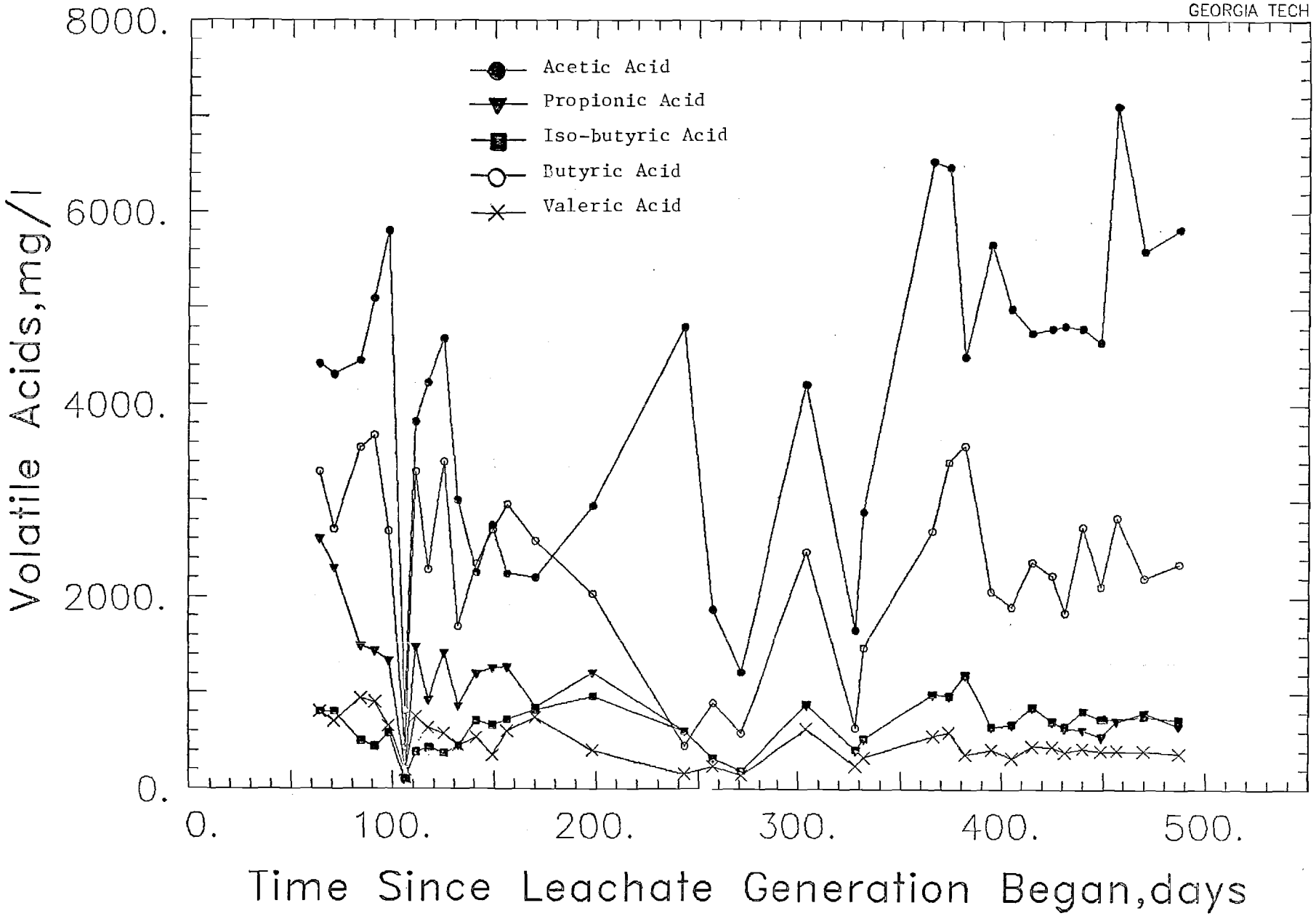


Figure 15. Individual Volatile Fatty Acids Content of Leachate from the Single-Pass Cell

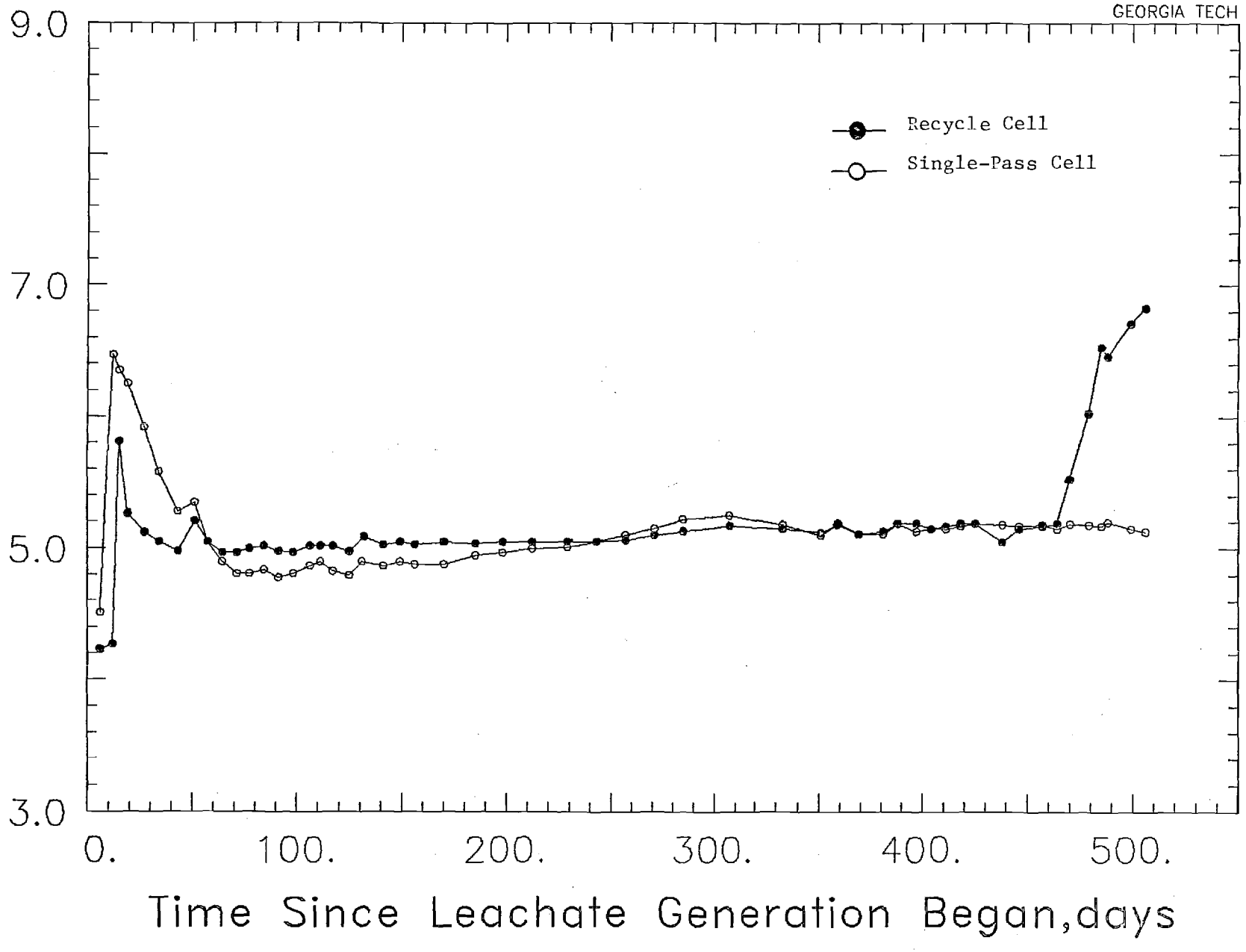


Figure 16. pH of Leachate

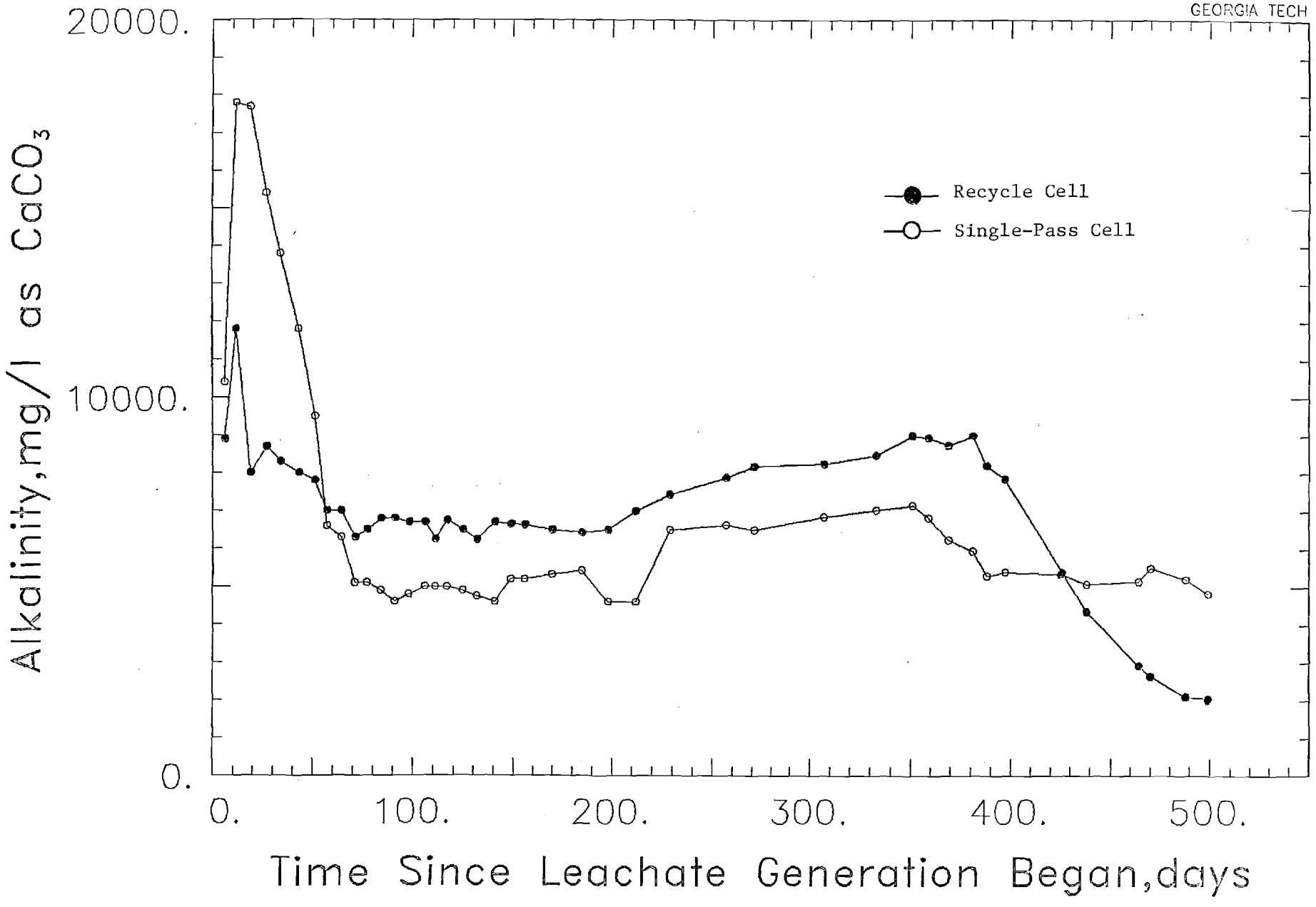


Figure 17. Total Alkalinity of Leachate

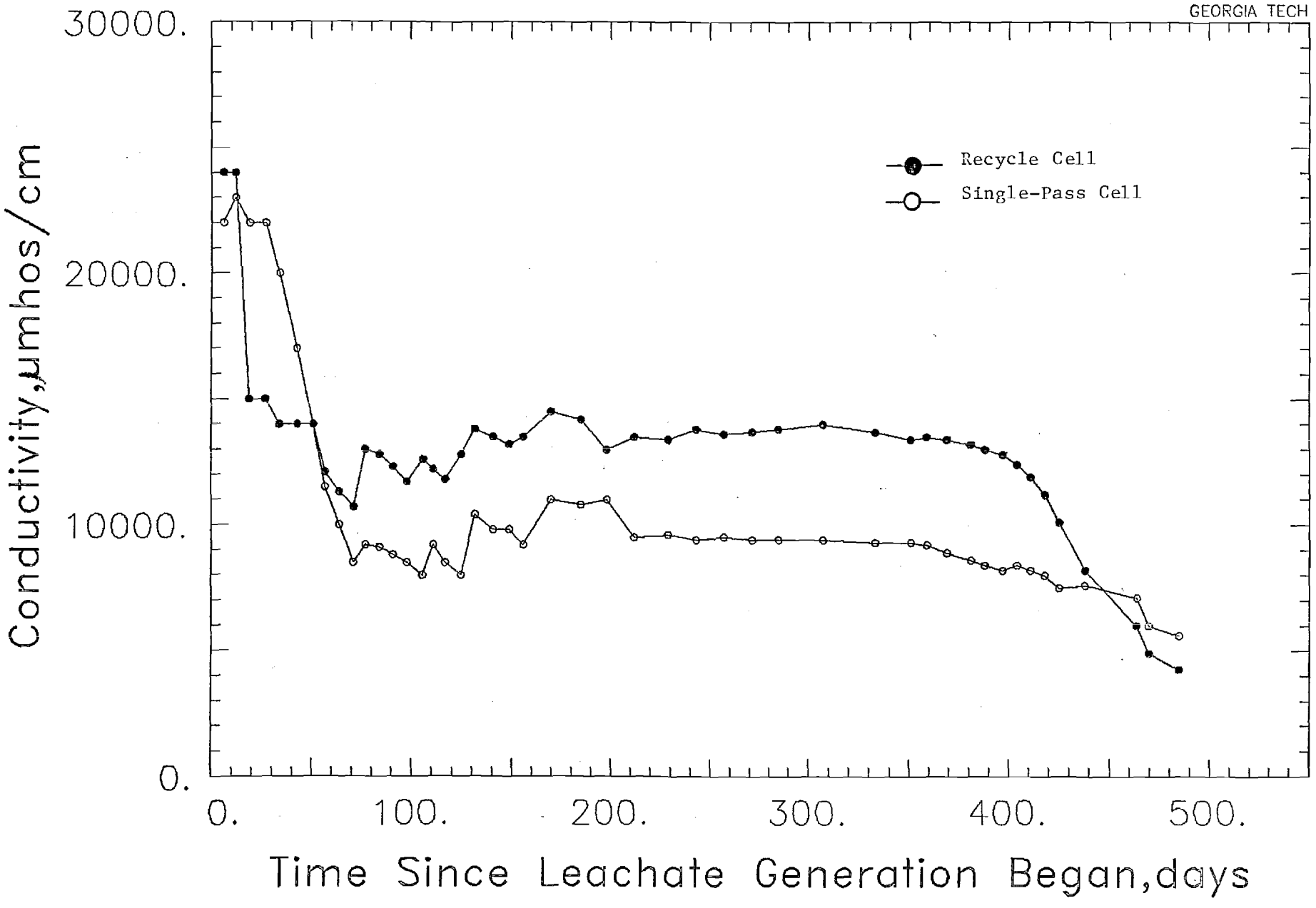


Figure 18. Conductivity of Leachate

The results of Oxidation-Reduction Potential (ORP) measurements on leachate from both cells are presented in Tables 10 and 11 and Figure 19. The negative ORP values indicate that both cells were operating under reducing conditions conducive to anaerobic biological stabilization. However, the magnitude of those values as measured were not as negative as generally reported for active methane fermentation and required for complete transformation of sulfates and sulfites to sulfides (ORP values of less than -200mV E_c). This higher ORP behavior was considered more of an analytical problem since sulfides were present in low concentrations (0.2 - 0.5mg/ℓ) consequenced also by their precipitation with heavy metals. Moreover, the decreasing ORP trend for the recycle cell coincided with the onset of active methane fermentation and accelerated stabilization of leachate organics as the cell environment became more highly reducing.

To further support this concept, leachate samples were also analyzed for selected metals often found to be present in the solid waste and/or having potentially adverse environmental or health impacts. The metal analyses included cadmium (Cd), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), nickel (Ni), sodium (Na) and zinc (Zn). Since cadmium was not detected in leachate samples during the first few months and only low concentrations of chromium were detected in the initial samples during this same period (Table 14), analyses for these metals in subsequent samples were discontinued.

Results of analyses for the remaining six metals are presented in Tables 15 and 16 and Figures 20 through 25 for both cells. All of the metals, with the exception of iron, showed an initial rapid decrease in concentration which was attributable to dilution of leachate in the

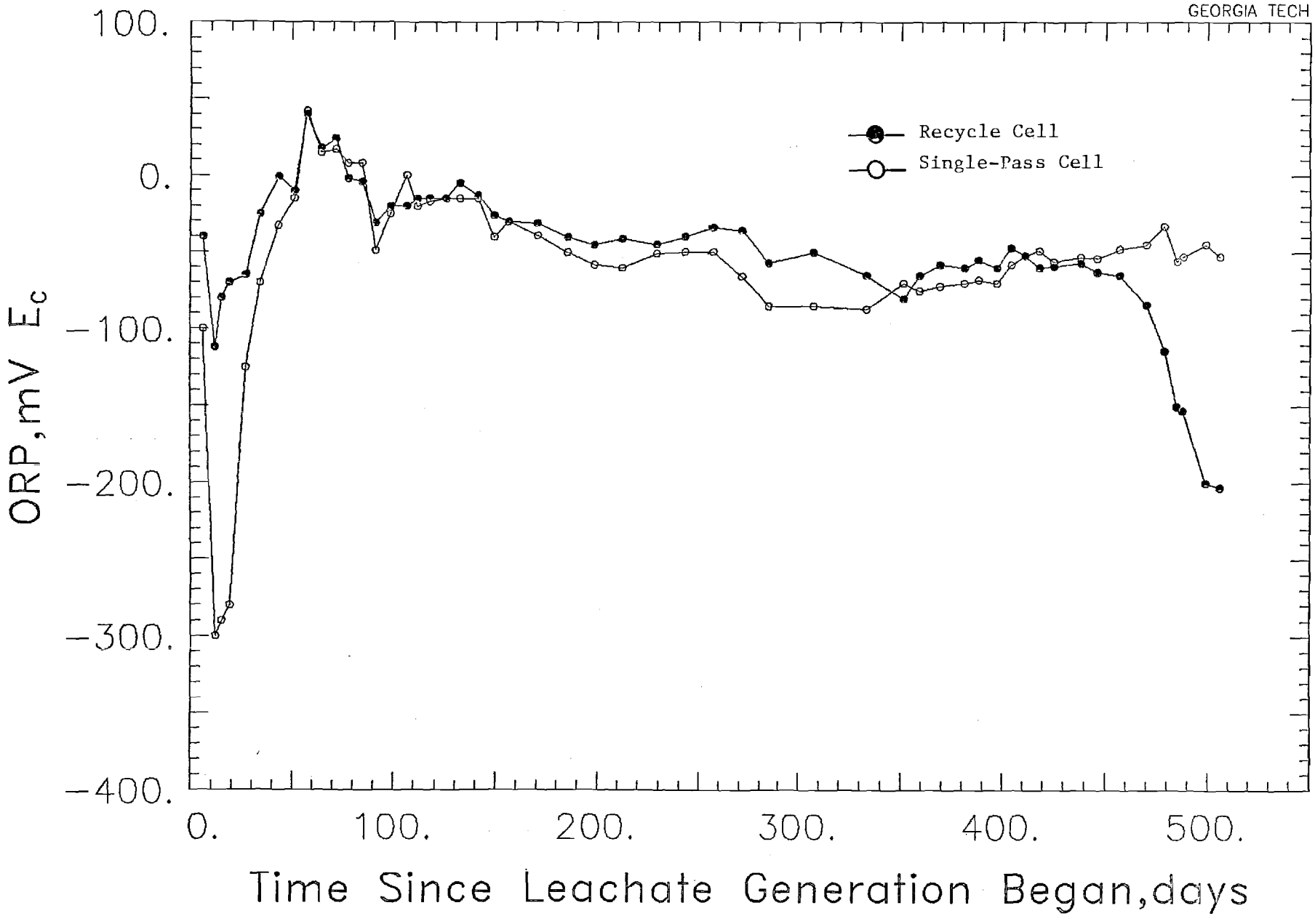


Figure 19. Oxidation - Reduction Potential of Leachate

Table 14. Results of Analyses for Cadmium and Chromium in Leachate Samples from the Recycle and Single-Pass Cells

Sampling Day	Cadmium, mg/ℓ		Chromium, mg/ℓ	
	Recycle Cell	Single-Pass Cell	Recycle Cell	Single-Pass Cell
12	ND*	ND	1.5	1.5
27	ND	ND	0.8	ND
43	ND	ND	0.8	ND
58	ND	ND	ND**	ND
71	ND	ND	ND	ND
85	ND	ND	ND	ND

*None Detected; Detection Limit, 0.5 mg/ℓ.
**None Detected; Detection Limit, 0.5 mg/ℓ.

Table 15. Results of Analyses for Iron, Magnesium, Manganese, Nickel, Sodium and Zinc in Leachate Samples from the Recycle Cell

Sampling Day	Fe, mg/l	Mg, mg/l	Mn, mg/l	Ni, mg/l	N_a, mg/l	Zn, mg/l
12	234	495	84	2.4	1300	153
43	578	200	48	2.1	600	39
71	450	150	36	1.8	500	30
98	558	200	35	1.8	500	30
125	519	200	34	1.8	550	30
156	684	200	32	1.8	500	27
212	396	190	43	1.3	550	19
271	1014	180	49	1.4	630	19
285	1014	165	52	1.6	630	22
351	1114	168	50	1.3	600	18
369	1056	168	54	1.3	670	20
425	972	160	20	0.6	600	9
460	468	152	7	0.3	590	2
488	360	135	2	0.2	520	< 1
507	94	122	<1	0.5	640	< 1

Table 16. Results of Analyses of Iron, Magnesium, Manganese, Nickel, Sodium and Zinc in Leachate Samples from the Single-Pass Cell

Sampling Day	Fe, mg/l	Mg, mg/l	Mn, mg/l	Ni, mg/l	Na, mg/l	Zn, mg/l
12	756	500	126	3.9	2000	174
43	432	300	90	2.7	1100	150
71	425	120	30	1.2	500	87
98	413	100	19	0.9	500	54
125	576	100	20	0.9	400	36
156	882	100	18	0.5	300	27
212	1188	83	26	0.6	191	21
271	1170	105	28	0.3	195	13
285	1482	120	30	0.7	203	14
351	1628	105	34	0.6	216	24
369	1430	90	26	0.7	139	25
425	1296	81	16	0.3	92	8
460	1248	68	20	0.4	87	11
488	1296	70	16	0.2	80	10
507	1062	68	14	0.6	68	10

Table 17. Ammonia and Ortho-Phosphate Concentrations in Leachates from the Recycle and Single-Pass Cells

Sampling Day	Recycle Cell		Single-Pass Cell	
	Ammonia, mg/l NH_3	Ortho-Phosphate, mg/l $PO_4^{\equiv}$	Ammonia, mg/l NH_3	Ortho-Phosphate, mg/l $PO_4^{\equiv}$
212	650	6.6	950	1.1
271	-	2.0	-	1.1
317	725	-	950	-
352	-	15.0	-	1.5
381	900	-	950	-
425	550	4.8	400	2.8
471	104	-	475	-
488	110	-	475	-
506	60	-	460	-
509	-	6.6	-	1.1

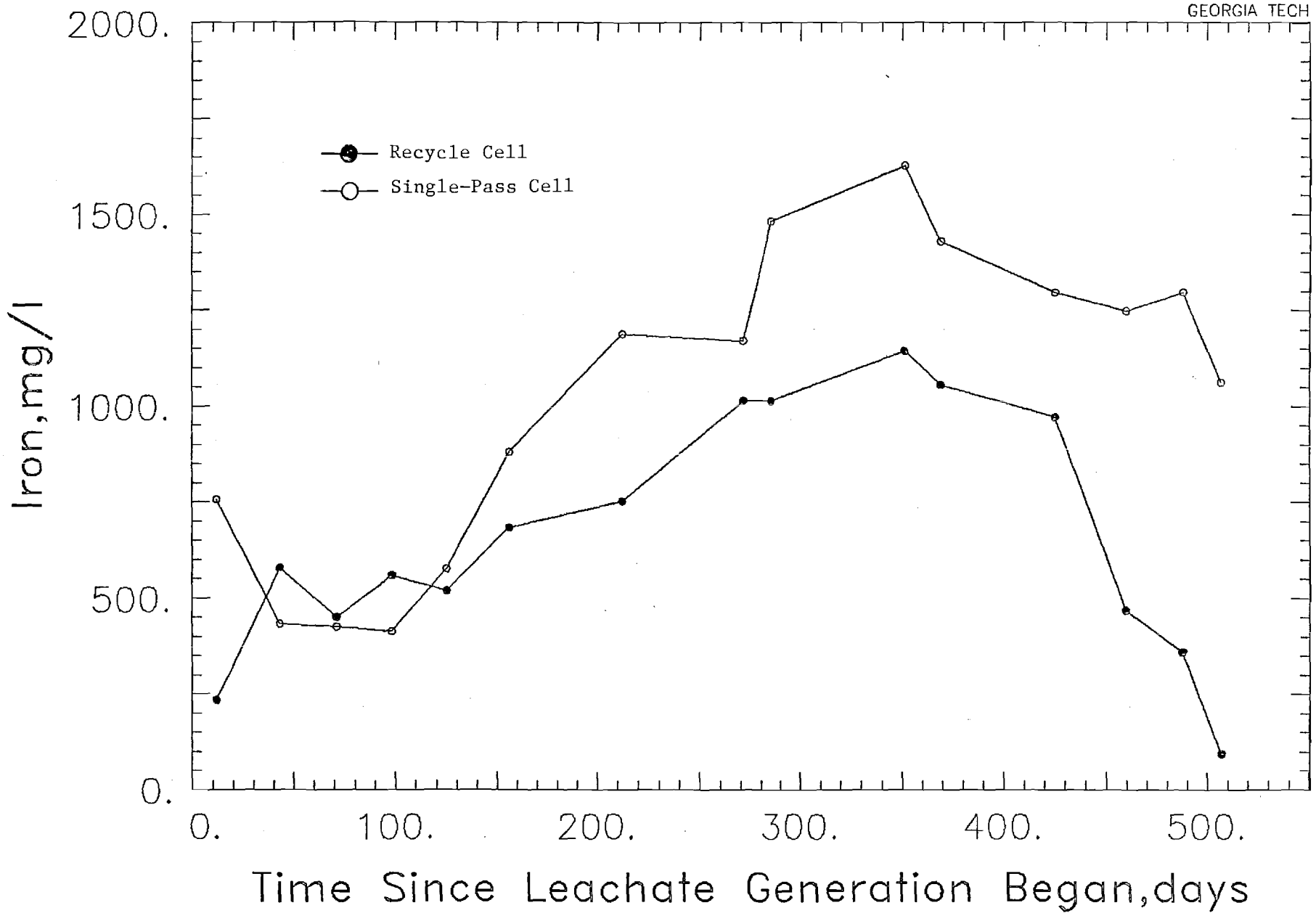


Figure 20. Concentration of Iron in Leachate

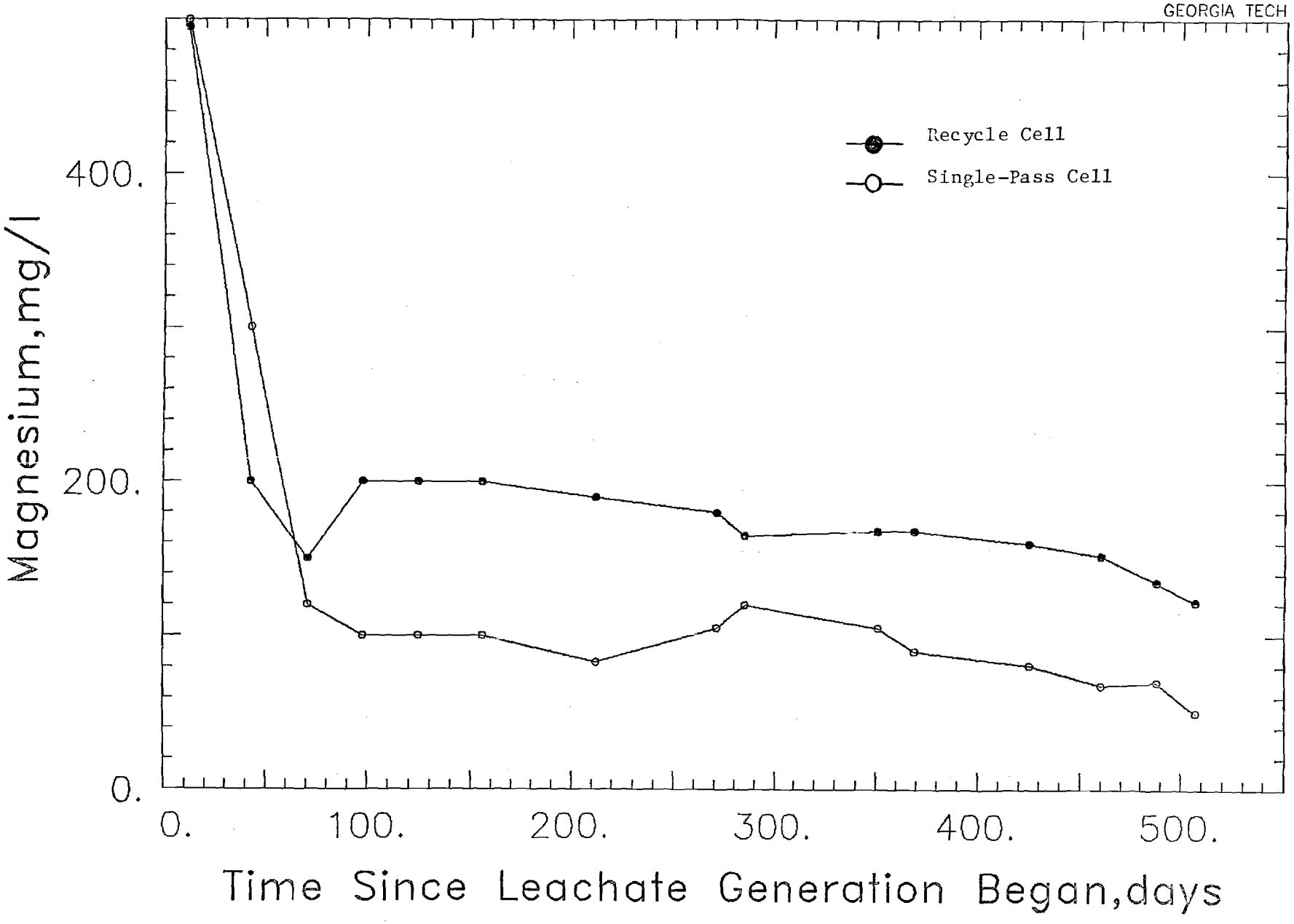


Figure 21. Concentration of Magnesium in Leachate

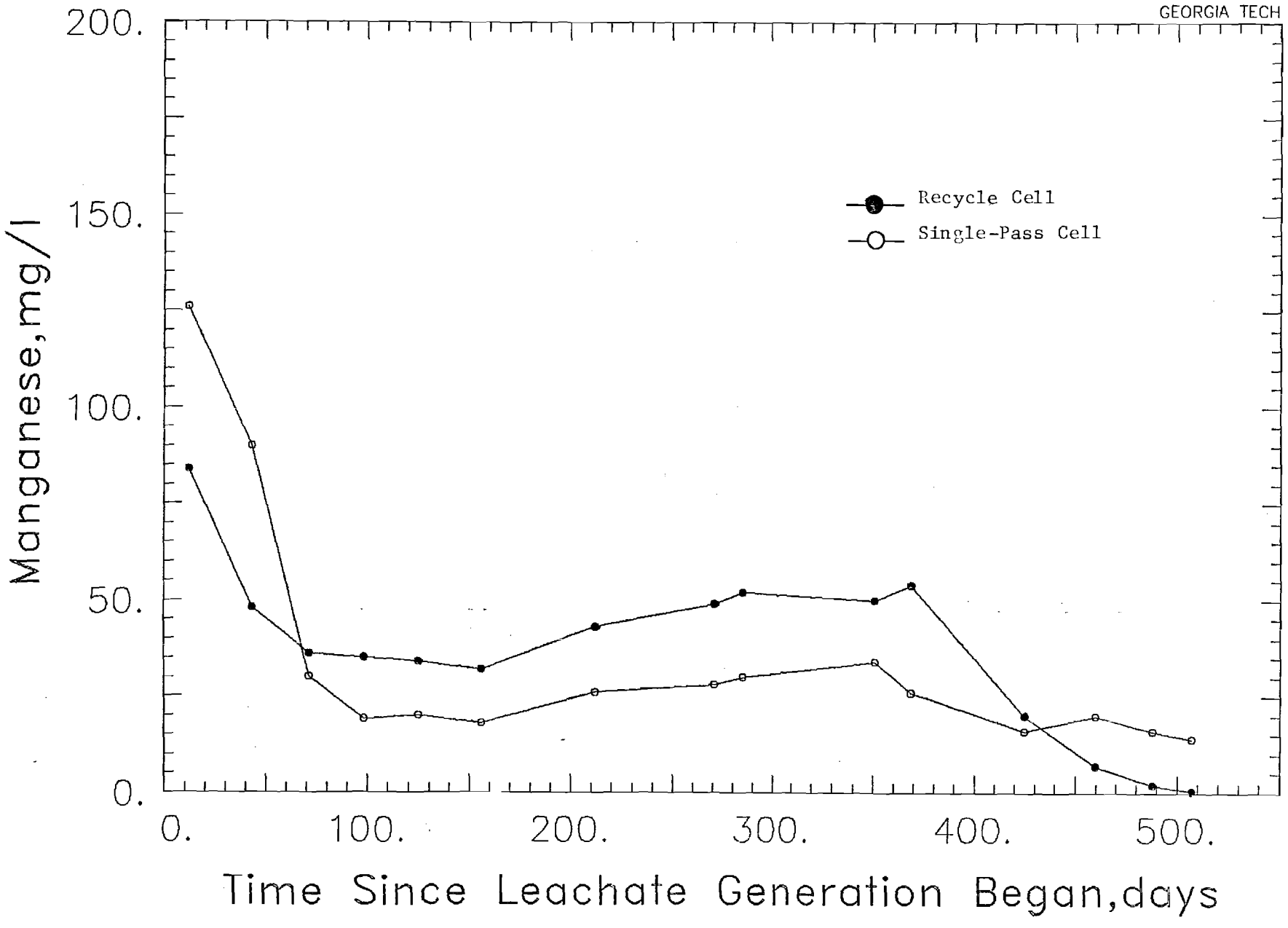


Figure 22. Concentration of Manganese in Leachate

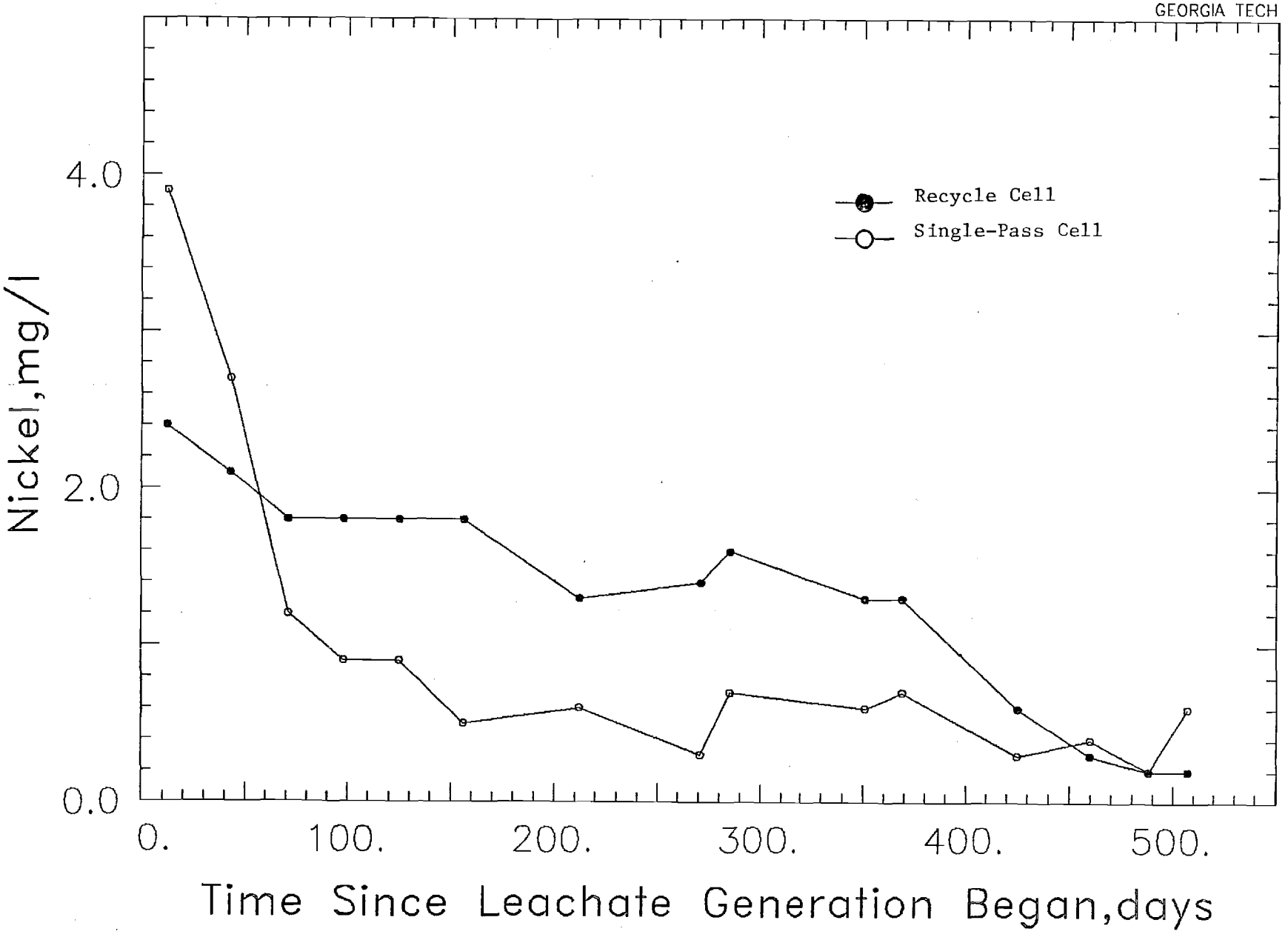


Figure 23. Concentration of Nickel in Leachate

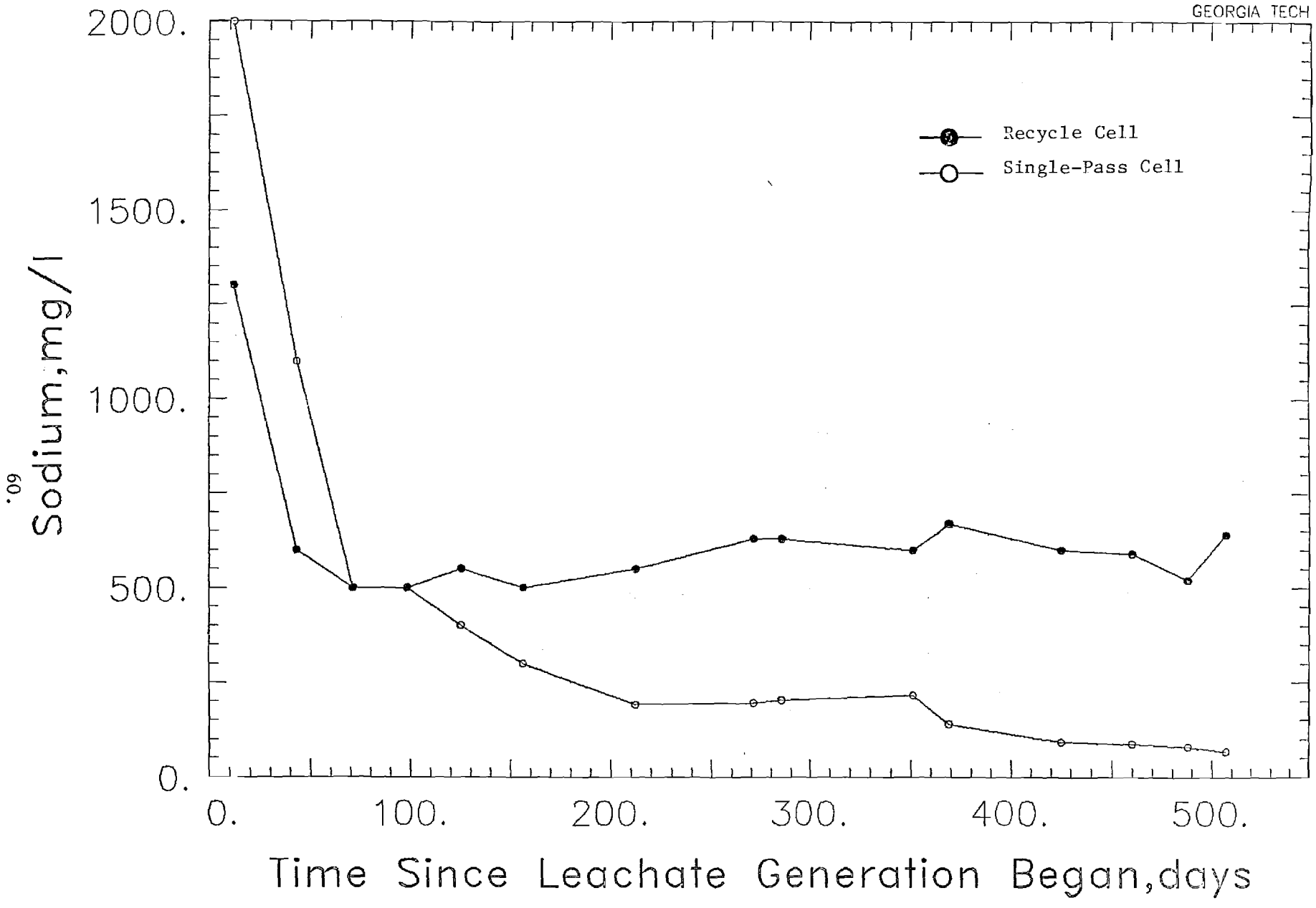


Figure 24. Concentration of Sodium in Leachate

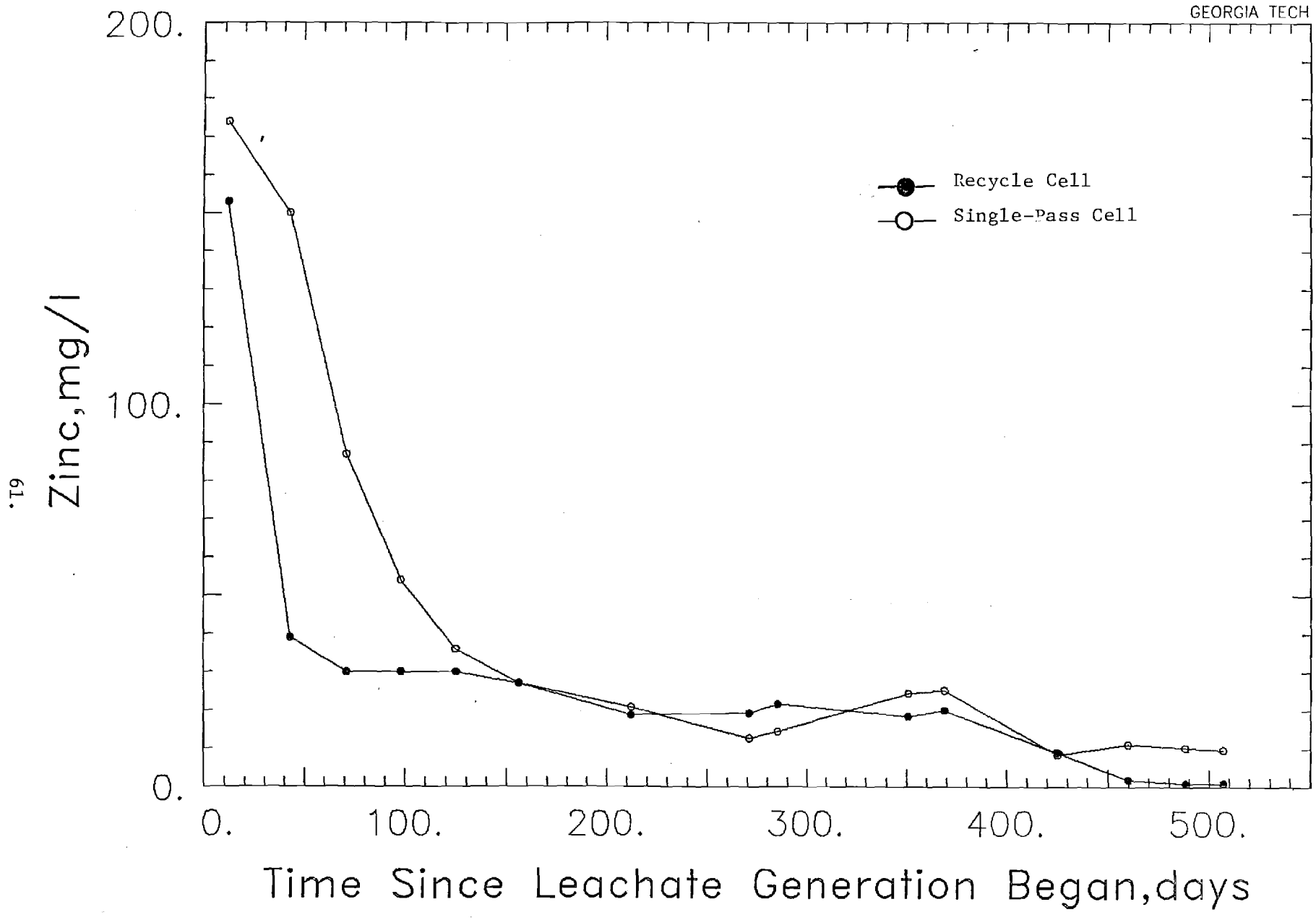


Figure 25. Concentration of Zinc in Leachate

recycle cell and wash-out of these metals in the single-pass cell as a result of moisture addition during this period. The increase of iron in both cells, which continued for approximately 350 days, probably resulted as a consequence of corrosion of this metal within the waste under the acidic conditions prevailing during this time in both cells. In the recycle cell, a further reduction in the concentration of all of these metals (with the exception of sodium) coincided with the period of rapid anaerobic stabilization, accelerated gas production and lowest ORP. Therefore, these reductions were attributed to the enhanced precipitation of the heavy metals as sulfides as more reducing conditions developed. their solubility decreased with increasing pH, and their removal was enhanced by filtration within the cell as the leachate was recycled. In contrast, decreases in concentrations of these metals in the single-pass cell were also attributable to the wash-out effect previously discussed.

Sodium, a highly soluble and conservative substance, was monitored to enable estimation of the dilution effects resulting from moisture addition to the cells. Accordingly, little change in sodium concentrations was observed in the recycle cell after moisture addition to this cell was discontinued, whereas, in the single-pass cell, a continuous decrease in sodium concentration of the leachate samples occurred and varied inversely with the total volume of moisture added to this cell.

In order to determine the possibility of nutrient limitations on the microbial activity within the landfill cells, analyses for ammonia nitrogen and phosphorus (ortho-phosphate) were performed on selected leachate samples (Table 17 and Figures 26 and 27). These

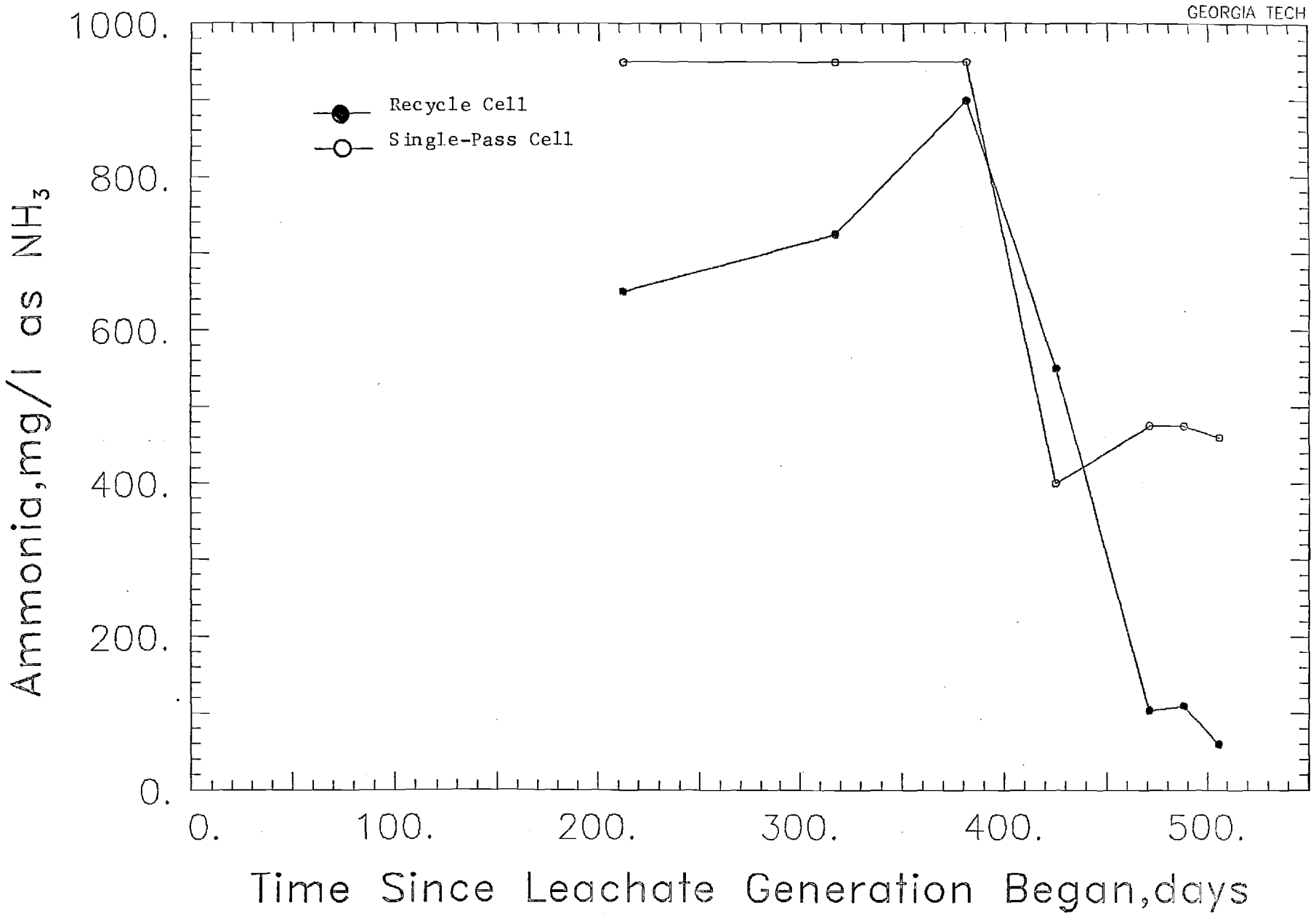


Figure 26. Concentration of Ammonia in Leachate

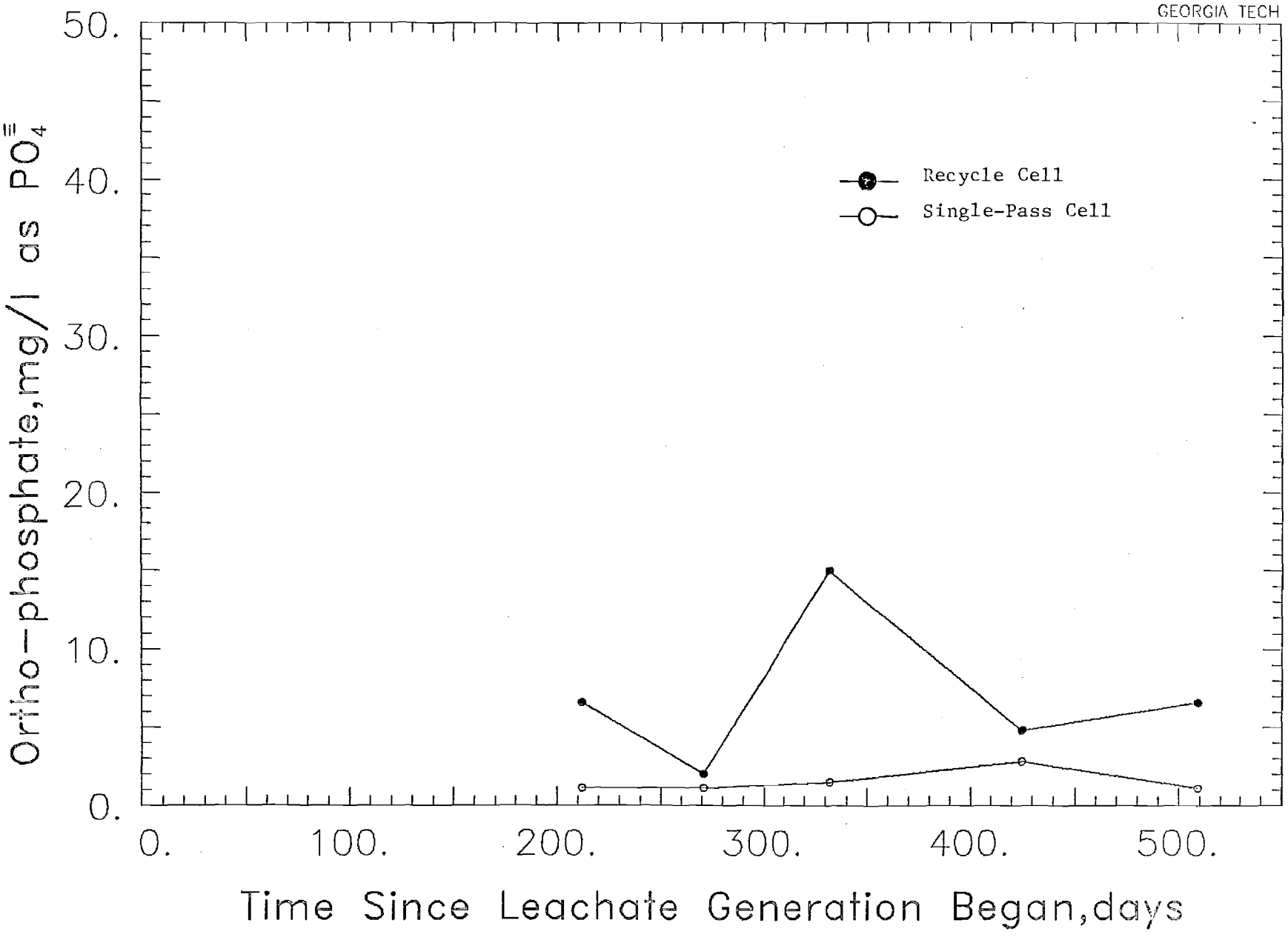


Figure 27. Concentration of Ortho-Phosphate in Leachate

results indicated that these nutrients were present in the cells throughout the experimental period and were, therefore, not considered limiting to microbial degradation of the waste. The decrease in ammonia (Figure 26) in the recycle cell corresponded to the utilization of nitrogen during the period of accelerated microbial stabilization within the cell. The low concentrations of phosphorus in the leachate from the single-pass cell may result in eventual phosphorus limitation within this cell due to the continuous washout of organics and nutrients from this cell with additional moisture addition. Such a nutrient limitation could reduce the opportunity for biodegradation and gas production within both cells.

Gas Production and Composition. Cumulative gas production for both cells is presented in Table 18 and Figure 28. The lack of any significant gas production during the first 350 days by both systems indicated that acid fermentation was dominant and conversion of acids to CH_4 and CO_2 had not yet been achieved. However, subsequent to the addition of digested sludge to both cells, an increase in gas production in the recycle cell was observed. Although gas production data for the single-pass cell are not available for this latter period due to the development of a gas leak in this cell, gas production in the recycle cell increased commensurate with reduction of volatile acids (and COD, TOC and BOD_5) and increase in pH.

To emphasize this relationship, daily gas production from the recycle cell, presented in Table 19 and Figure 29, indicates that the majority of gas production occurred during a relatively short period of approximately three months and coincided with the period of most rapid stabilization. Composition of the gas produced by the recycle cell (Table 20 and Figure 30) showed a gradual increase in CH_4 from 27%

Table 18. Cumulative Gas Production in Recycle and Single-Pass Cells

Time Days	Gas Production, liters per dry kg of Solid Waste @ STP: Recycle Cell	Single - Pass Cell	Time Days	Gas Production, liters per dry kg of Solid Waste @ STP: Recycle Cell	Single-Pass Cell
6	0.69	0.19	243	1.94	4.69
12	1.21	1.49	257	1.96	4.69
19	1.46	2.54	271	2.05	4.69
27	1.56	3.01	285	2.05	4.69
34	1.64	3.15	307	2.05	4.69
43	1.72	3.36	333	2.05	4.69
51	1.76	3.53	351	2.05	4.69
58	1.76	3.53	359	2.52	4.92
64	1.76	3.53	369	3.12	-*
71	1.76	3.67	381	4.21	-
77	1.76	3.72	388	6.48	-
84	1.76	3.74	397	11.78	-
91	1.76	3.91	404	16.95	-
98	1.76	3.93	411	23.83	-
106	1.76	4.06	418	30.52	-
111	1.78	4.09	425	36.77	-
117	1.79	4.17	438	47.75	-
125	1.79	4.25	442	50.58	-
132	1.79	4.25	446	53.74	-
141	1.79	4.35	457	62.04	-
149	1.76	4.45	464	65.56	-
156	1.79	4.45	470	67.19	-
170	1.79	4.53	479	69.22	-
185	1.79	4.64	485	70.44	-
198	1.79	4.64	493	71.32	-
212	1.79	4.64	510	72.48	-
229	1.85	4.67			

*Gas Leak in Cell

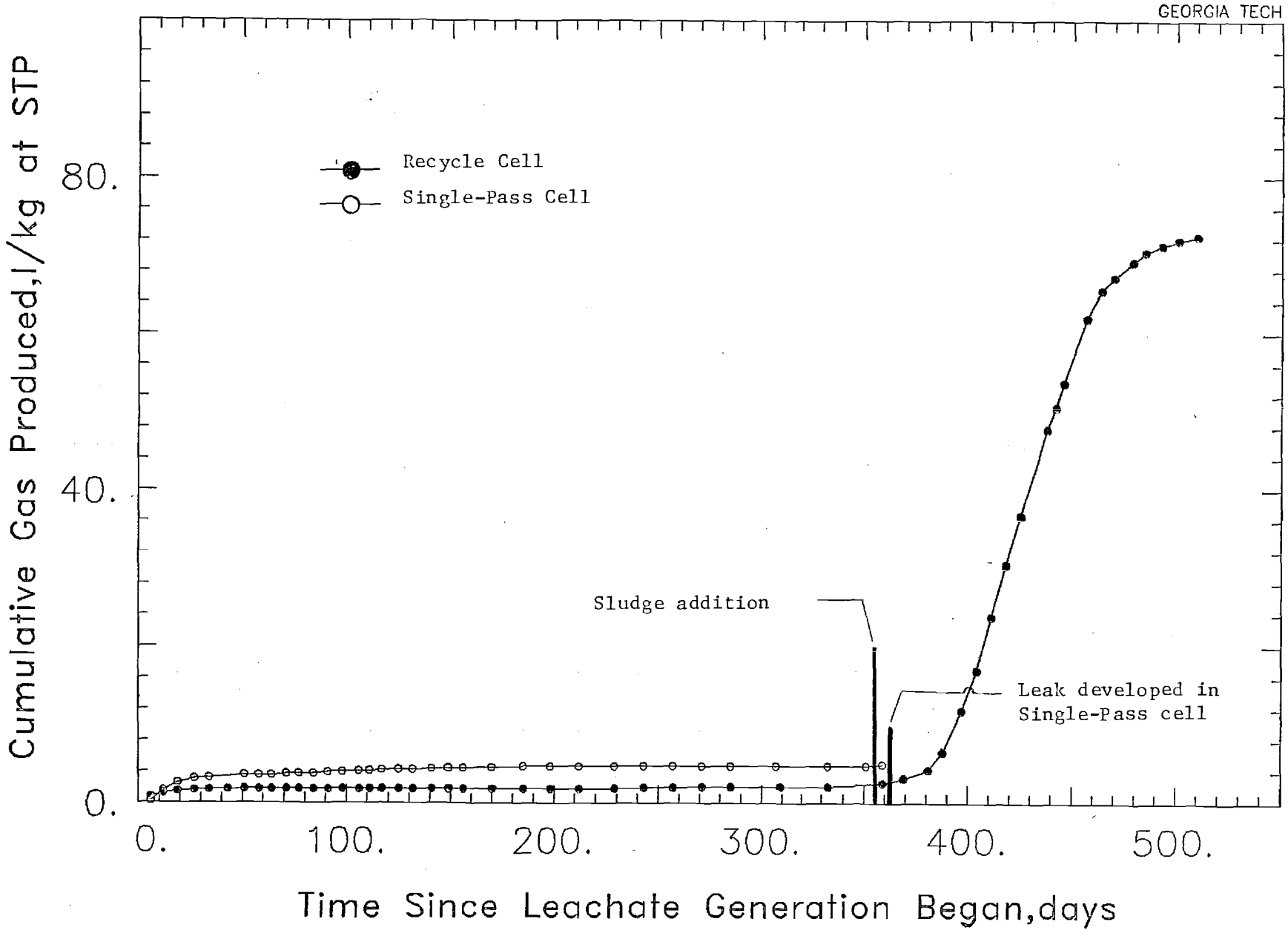


Figure 28. Cumulative Gas Production from Simulated Landfill Cells

Table 19. Daily Gas Production by Recycle Cell After Sludge Addition

Time, days	Gas Produced, l/kg solid waste*	Time, days	Gas Produced, l/kg solid waste*	Time, days	Gas Produced, l/kg solid waste*
355	0.143	395	0.584	435	0.909
356	0.092	396	0.652	436	0.954
357	0.086	397	0.716	437	0.729
358	0.046	398	0.702	438	0.637
359	0.103	399	0.662	439	0.645
360	0.053	400	0.685	440	0.711
361	0.087	401	0.730	441	0.723
362	0.036	402	0.771	442	0.753
363	0.041	403	0.858	443	0.794
364	0.111	404	0.830	444	0.784
365	0.202	405	0.923	445	0.788
366	0.068	406	0.920	446	0.793
367	-	407	1.034	447	0.814
368	-	408	0.958	448	0.748
369	-	409	0.886	449	0.765
370	-	410	0.977	450	0.769
371	-	411	0.982	451	0.706
372	-	412	0.989	452	0.610
373	-	413	1.050	453	0.598
374	-	414	1.046	454	0.576
375	-	415	1.016	455	0.594
376	0.198	416	0.971	456	0.612
377	0.111	417	0.915	457	0.593
378	0.106	418	0.900	458	0.555
379	0.229	419	0.892	459	0.507
380	0.207	420	0.876	460	0.537
381	0.246	421	0.851	461	0.537
382	0.293	422	0.895	462	0.537
383	0.208	423	0.815	463	0.427
384	0.276	424	0.845	464	0.421
385	0.288	425	0.876	465	0.366
386	0.386	426	0.854	466	0.349
387	0.383	427	0.846	467	0.260
388	0.437	428	0.838	468	0.256
389	0.470	429	0.749	469	0.193
390	0.604	430	1.104	470	0.194
391	0.526	431	0.773	471	0.170
392	0.492	432	0.810	472	0.146
393	0.584	433	0.856	473	0.220
394	0.555	434	0.912	474	0.206

(Continued)

Table 19. (Continued)

Time, days	Gas Produced, l/kg solid waste*	Time, days	Gas Produced, l/kg solid waste*	Time, days	Gas Produced, l/kg solid waste*
475	0.257	487	0.155	499	0.090
476	0.244	488	0.102	500	0.099
477	0.247	489	0.072	501	0.079
478	0.247	490	0.085	502	0.044
479	0.280	491	0.077	503	0.048
480	0.276	492	0.103	504	0.058
481	0.226	493	0.100	505	0.061
482	0.187	494	0.075	506	0.043
483	0.174	495	0.084	507	0.044
484	0.169	496	0.094	508	0.061
485	0.184	497	0.088	509	0.075
486	0.178	498	0.079	510	0.039

*On dry weight basis.

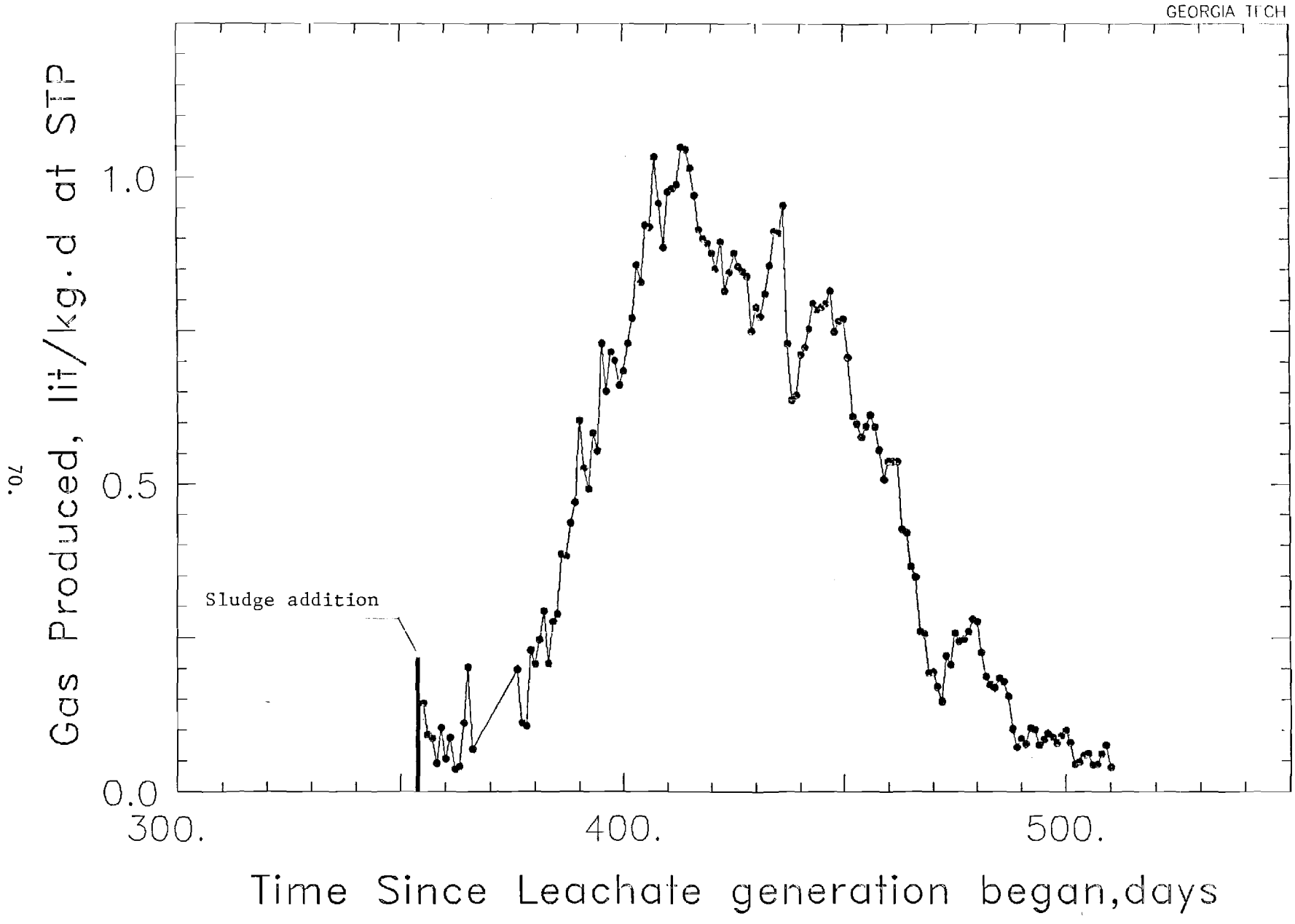


Figure 29. Daily Cas Production from Recycle Cell After Sludge Addition

Table 20. Composition of Gas from Recycle and Single-Pass Cells After Addition of Sludge

Sampling Day	Recycle Cell Gas Composition, %					Single-Pass Cell Gas Composition, %				
	N_2,	CO_2,	O_2,	H_2,	CH_4	N_2,	CO_2,	O_2,	H_2,	CH_4
359	35	38	<1	ND	27	43	41	<1	ND	16
362	33	39	<1	ND	28	44	38	<1	ND	18
366	28	39	<1	ND	33	44	38	<1	ND	18
369	25	39	<1	ND	36	42	39	<1	ND	19
373	27	38	<1	ND	35	40	38	2	ND	20
376	33	38	<1	ND	29	41	37	1	ND	21
379	26	40	<1	ND	34	38	39	<1	ND	23
383	23	39	<1	ND	38	36	40	<1	ND	24
386	14	40	<1	ND	46	33	43	<1	ND	25
390	10	41	ND*	2.0	48	31	43	<1	ND	26
394	8	40	ND	ND	52	31	41	<1	ND	28
404	3	39	ND	ND	59	30	38	<1	ND	32
410	4	39	ND	ND	57	31	36	<1	ND	33
415	8	35	ND	ND	57	–	–	–	–	–
418	1	42	ND	ND	57	22	45	<1	ND	33
423	<1	43	ND	ND	57	21	45	ND	ND	34
429	5	42	ND	ND	53	25	41	ND	ND	34
436	3	42	ND	ND	55	24	41	ND	ND	35
442	2	43	ND	ND	55	25	40	ND	ND	35
458	4	40	ND	ND	56	25	38	ND	ND	37
466	3	42	ND	ND	56	23	39	ND	ND	42
478	1	44	ND	ND	54	21	42	ND	ND	37
493	4	43	ND	ND	53	21	41	ND	ND	39

*Not Detected.

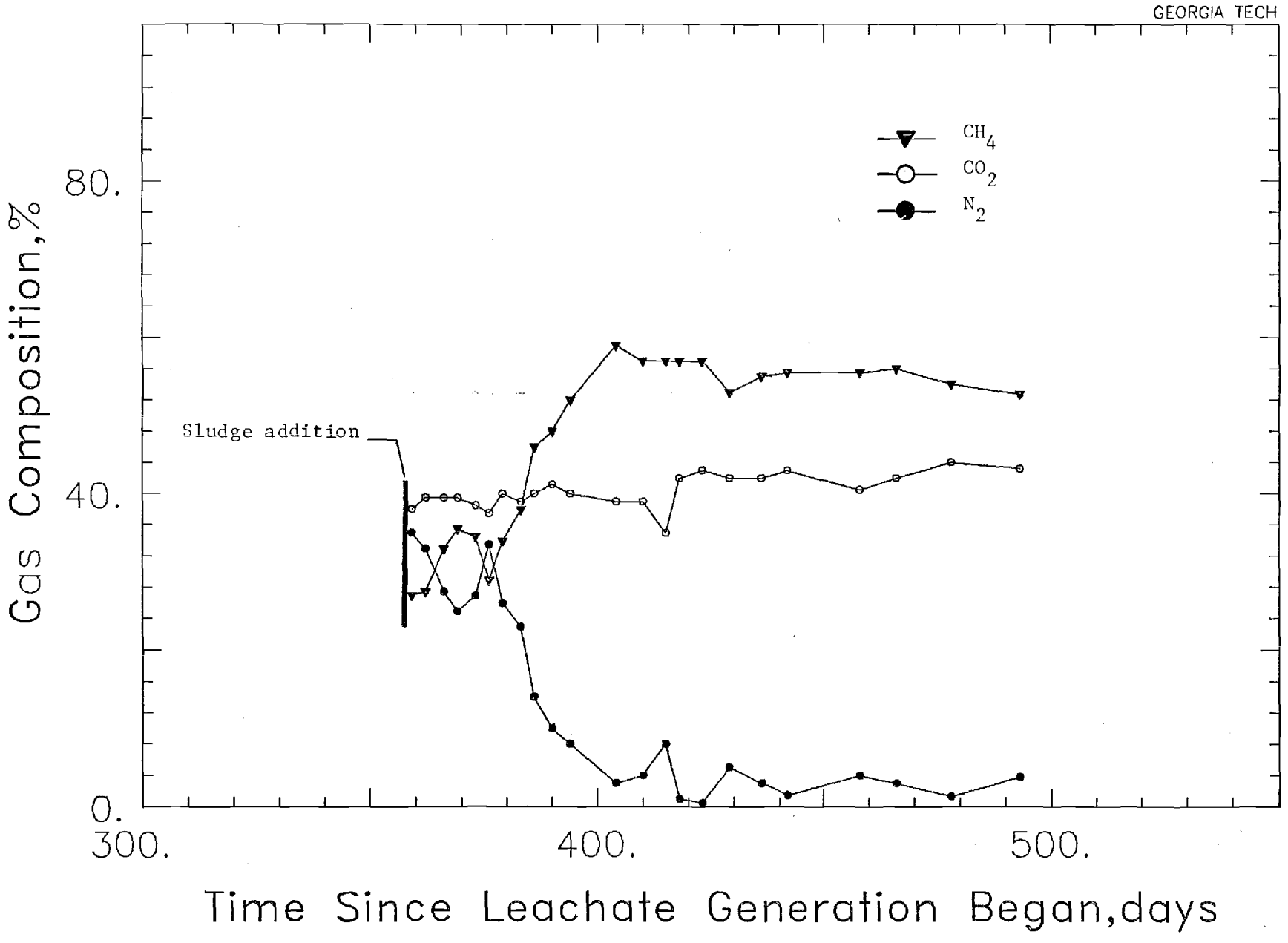


Figure 30. Composition of Gas from Recycle Cell After Sludge Addition

to approximately 56% which is indicative of efficient anaerobic biological stabilization by methane fermentation. Total gas production was approximately 72 ℓ/dry kg of solid waste; total methane production was approximately 40 ℓ/dry kg of solid waste.

The composition of gas in the single-pass cell (Table 20 and Figure 31) showed an increase in CH_4 content from approximately 17% to 38% with a corresponding decrease in N_2 content from 44% to 20%. This indicated that, although anaerobic biological stabilization did occur in this cell, it apparently occurred at a very low rate since insufficient gas was produced to flush out the nitrogen present as residual in the cell from leak tests (nitrogen gas had been introduced under pressure into the cell in order to detect the presence of possible leaks in the system). Furthermore, corresponding decreases in volatile acids, COD, TOC, BOD_5 and changes in other indicator parameters (e.g., pH, ORP, alkalinity, etc.) reflective of active stabilization, were not observed.

Fate of Formaldehyde. Initial attempts to detect and quantify formaldehyde in the leachate were made using direct injection, packed column GC; direct aqueous injection, capillary column GC-MS; and, the chromatropic acid colorimetric methods. The results of these analyses are summarized in Table 21. The direct aqueous injection, packed column GC method produced poor separation of the formaldehyde peak from other peaks in both the samples and standards. This prevented reliable determination of formaldehyde concentrations and this method was, therefore, abandoned.

Formaldehyde was not detected in either leachate sample by direct aqueous injection capillary column GC-MS. This determination was made

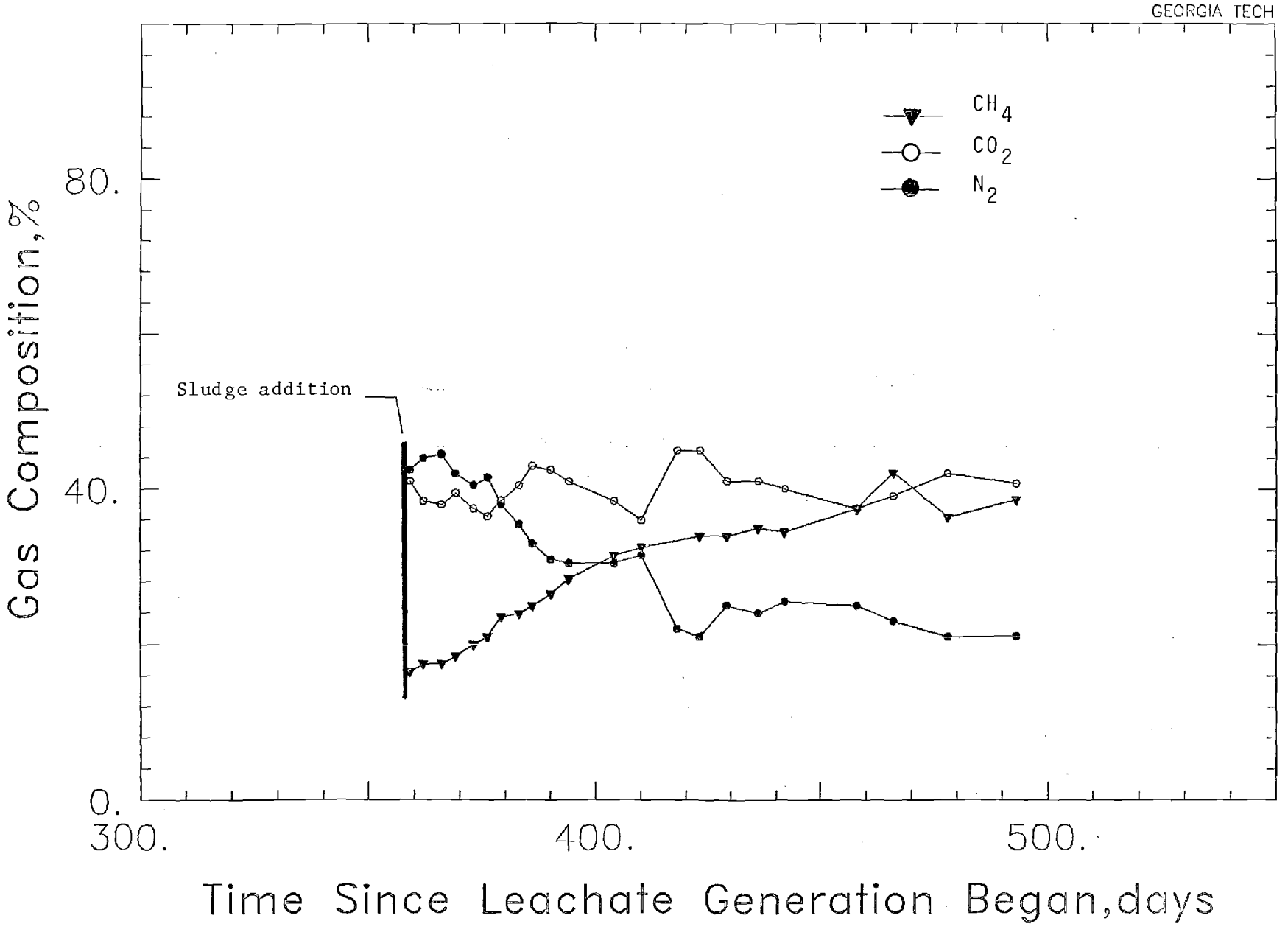


Figure 31. Composition of Gas from Single-Pass Cell After Sludge Addition

Table 21. Preliminary Results of the Determination of Formaldehyde in Leachate from the Single-Pass Simulated Landfill Cell by Gas Chromatography, Gas Chromatography-Mass Spectroscopy, and the Chromatropic Acid Methods

Analytical Method*	Sampling Date 8/7/82	Sampling Date 9/29/82	Comments
Direct Aqueous Injection Gas Chromatrographic Technique	-	-	Poor separation of the formaldehyde peak from other peaks in both samples and standards prevented reliable determination of formaldehyde directly from aqueous solutions.
Direct Aqueous Injection, Capillary Column Gas Chromatography-Mass Spectroscopy (GC-MS) Technique	ND**	ND**	Formaldehyde can be specifically identified with a detection limit of 100 mg/l. Therefore, formaldehyde was not present in the leachate in concentrations greater than 100 mg/l.
Chromatropic Acid, Colorimetric Method	270 mg/l	30 mg/l	A positive reaction with the reagent occurred and, if the color development was solely attributable to formaldehyde, significant concentrations of formaldehyde could be present in the leachate samples. Reliability decreases with complexity of mixture (e.g., leachate) due to interferences with positive reaction with the reagent. (Since the GC-MS method is not subject to such interferences and did not detect formaldehyde in concentrations above 100 mg/l, color development was at least partially attributable to the reaction of other constituents present in the leachate.) Therefore, the method was not reliable for the determination of formaldehyde in the complex leachate samples.

*See Appendix A for a more detailed description of these analytical methods.

**ND - Not detected.

by comparison of chromatograms of a formaldehyde standard solution with those of the leachate samples and the leachate samples spiked with formaldehyde (Figures 32 through 36, respectively). Although the direct aqueous injection, GC-MS method was able to positively identify formaldehyde, the detection limit was $\geq$ 100 mg/l. Consequently, this method only indicated that formaldehyde was not present in the leachate in concentrations greater than 100 mg/l.

Analysis of the leachate samples by the chromotropic acid colorimetric method resulted in a positive reaction with the reagent in both samples. The color intensity of the samples, if color development was only due to the reaction of formaldehyde with the chromotropic acid reagent, indicated a formaldehyde concentration of 270 mg/l and 30 mg/l in the leachate samples collected on Day 27 (8/07/82) and Day 80 (9/29/82), respectively. However, as previously indicated in Table 1, the reliability of this method decreases when used with complex mixtures due to interferences of other compounds present, i.e., those that can interfere with the formation and/or intensity of color development. Since the GC-MS method, which is most specific with respect to detecting the presence or absence of formaldehyde in concentrations of greater than 100 mg/l, did not detect any formaldehyde in the samples collected on 8/07/82, it could be concluded that the color development was at least partially attributable to the reaction of the reagent with other constituents present in the leachate. Hence, the method was not reliable for the determination of formaldehyde in the complex leachate samples.

Because of the limitations of each of these analytical methods for the determination of formaldehyde in leachate, no further analyses of

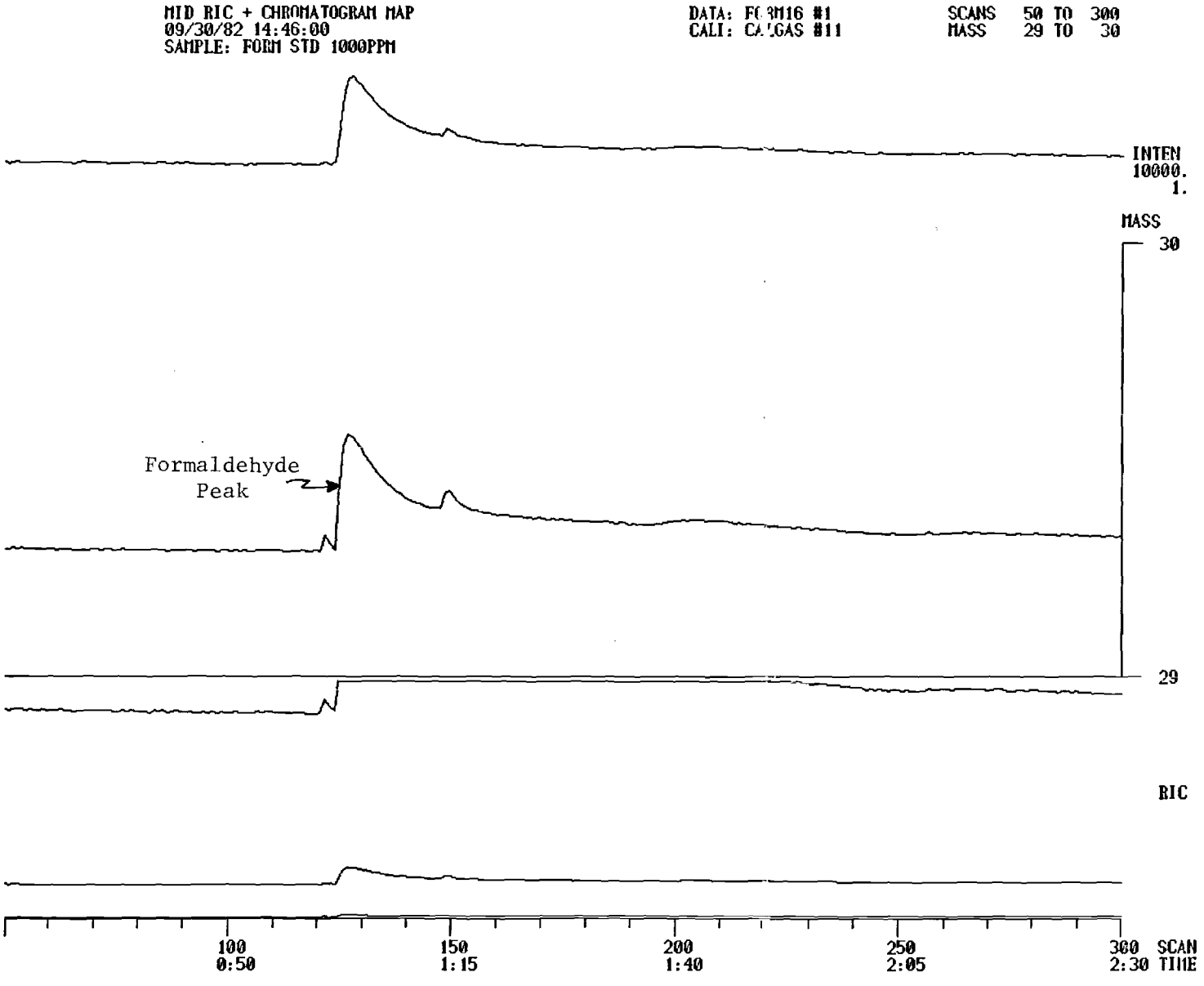


Figure 32. Fragmentogram of Formaldehyde Standard

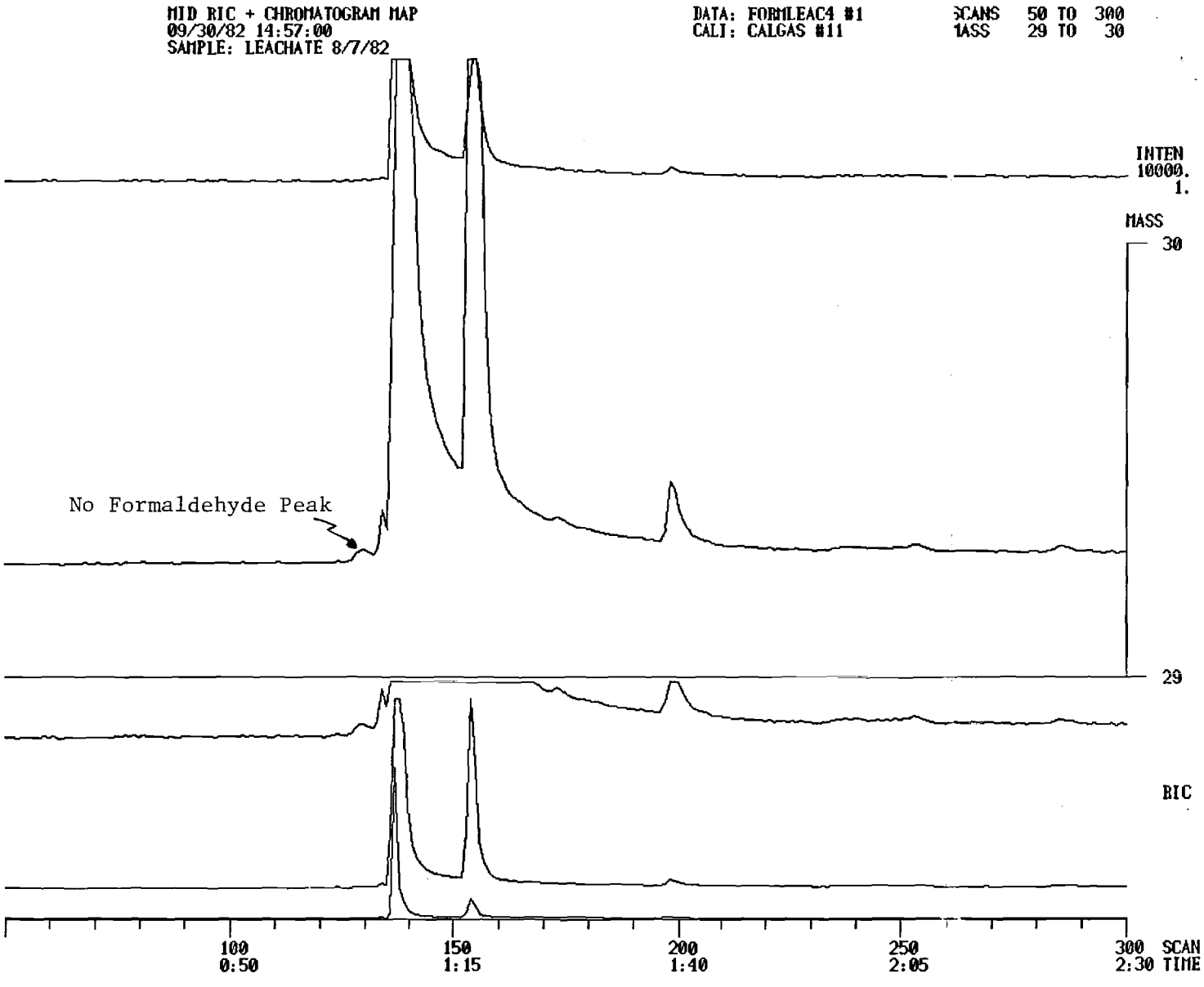


Figure 33. Fragmentogram of Formaldehyde in Leachate from Single-Pass Cell (8/07/82)

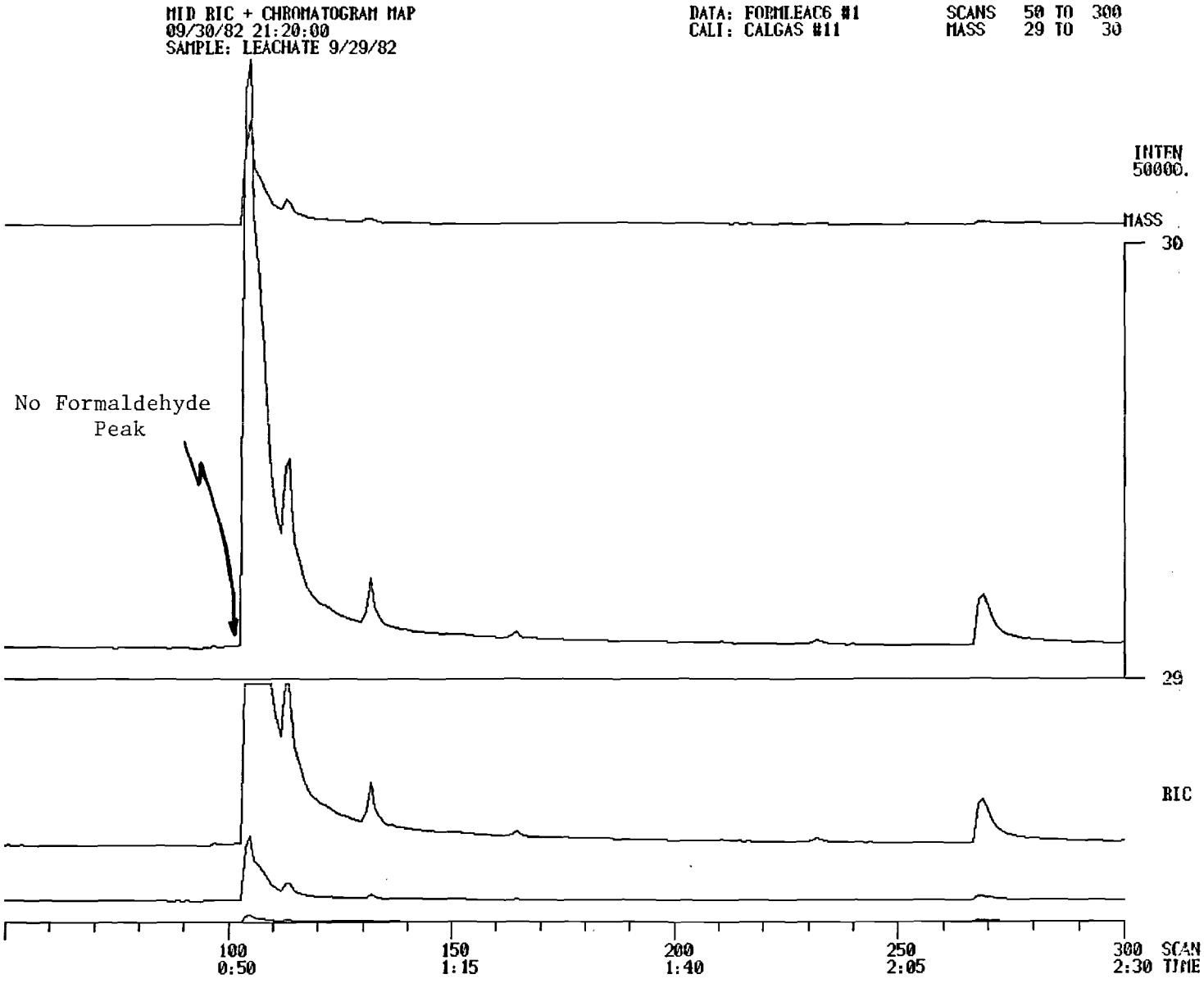


Figure 34. Fragmentogram of Formaldehyde in Leachate of Single-Pass Cell (9/29/82)

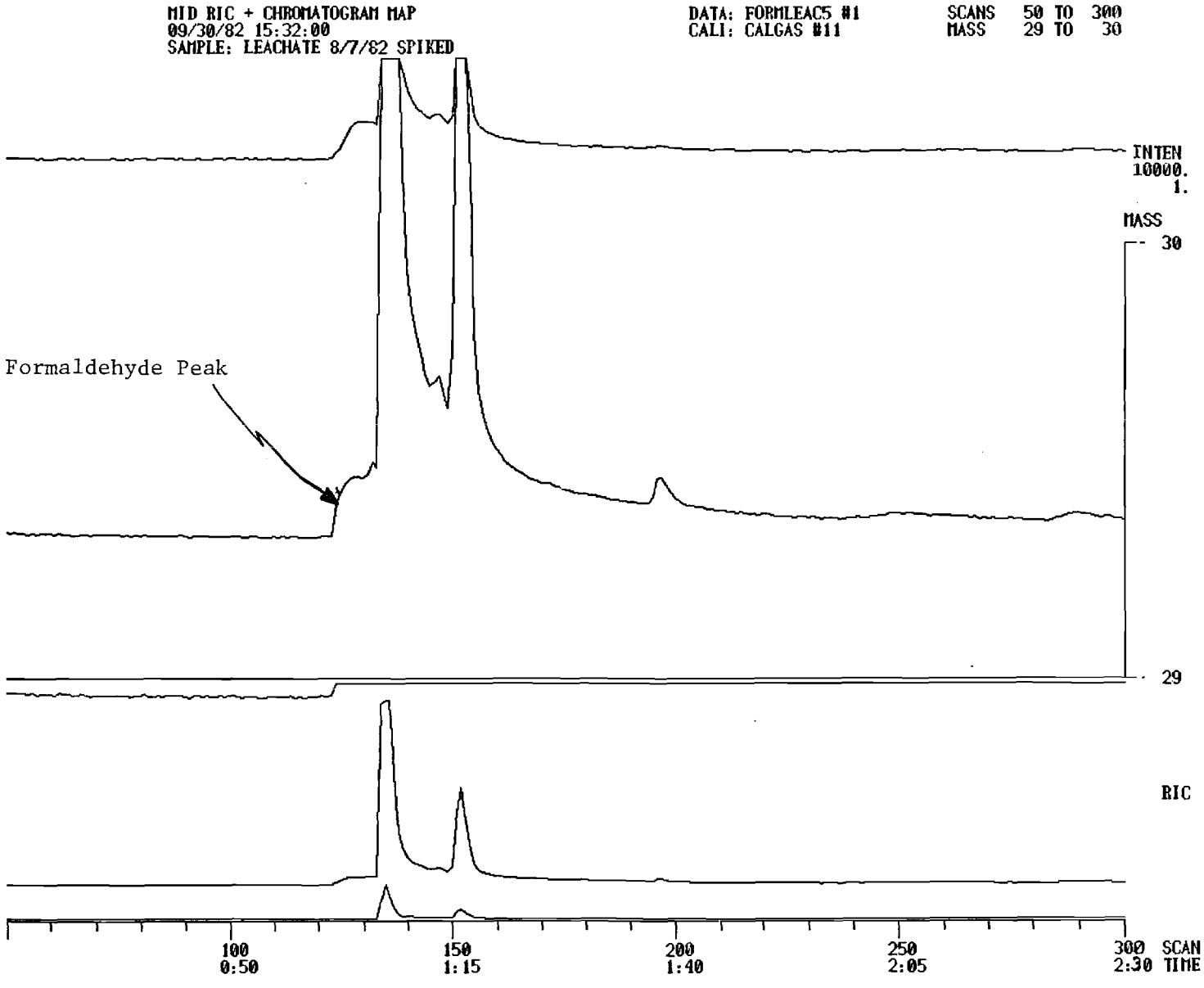


Figure 35. Fragmentogram of Formaldehyde in Spiked Leachate Sample from Single-Pass Cell (8/07/82)

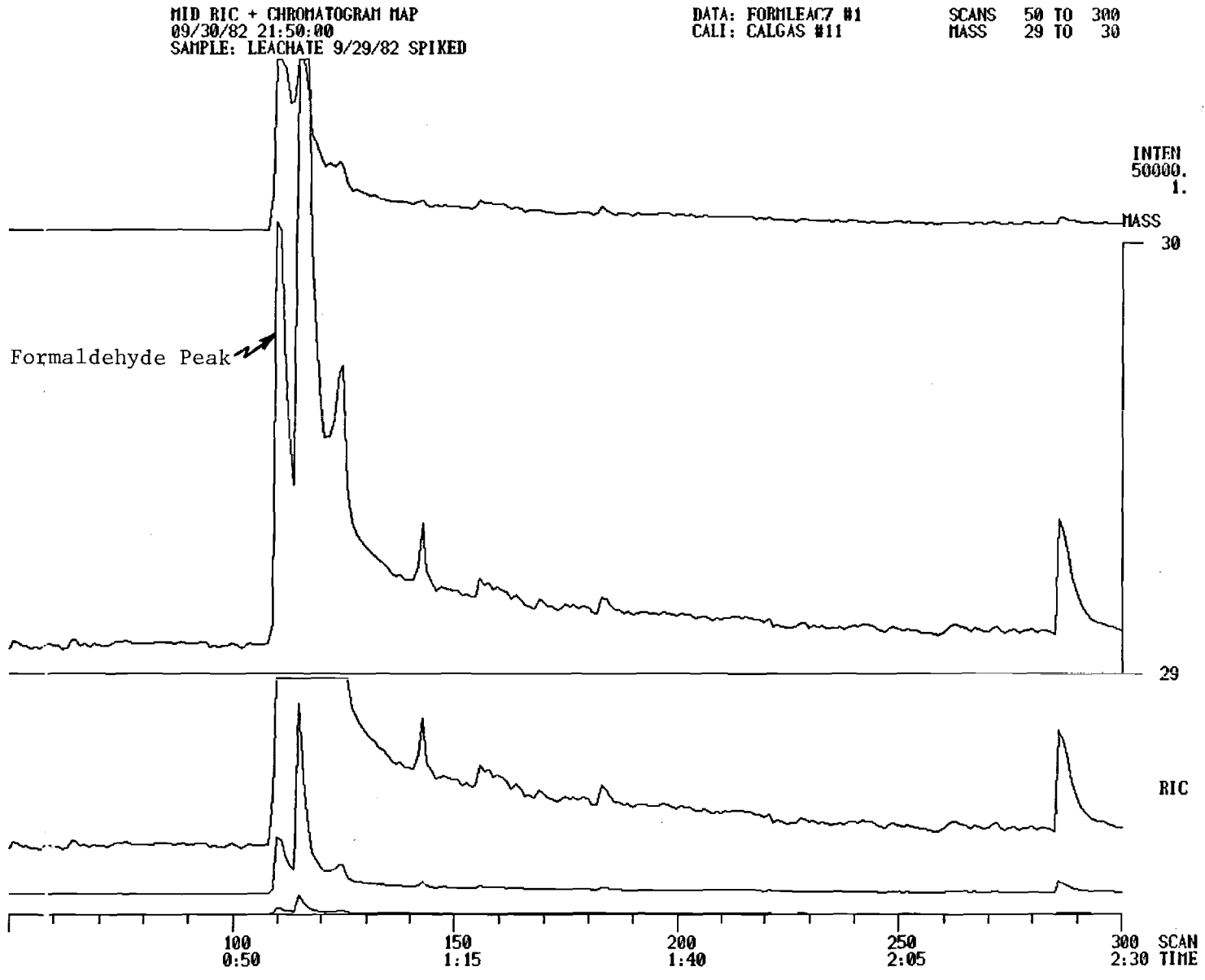


Figure 36. Fragmentogram of Formaldehyde in Spiked Leachate Sample from Single-Pass Cell (9/29/82)

leachate samples by these methods has been attempted. Therefore, subsequent analyses of leachate samples were performed by use of the DNPH derivatization method previously discussed.

Results of analyses for formaldehyde by the DNPH derivatization method are presented in Table 22 and Figure 37. Concentrations of formaldehyde measured in leachate samples from the recycle cell ranged from 30.4 to 16.8 mg/ℓ through Day 360, increased to approximately 42 mg/ℓ during the following 40 days, and then decreased rapidly to approximately 3 mg/ℓ at the end of the study period. The decreasing trend in formaldehyde concentration observed from Day 230 through Day 260, and subsequent increase during the next 40 days, was attributable to changes in the operation of the recycle cell (See Figure 4). Only intermittent recycle of small quantities of leachate was performed between Days 195 and 358, whereas subsequent to sludge addition, the cell was operated with daily recycle of gradually increasing volumes of leachate. This provided the opportunity for increased flushing of formaldehyde from the foam and resulted in an apparent increase in formaldehyde in the leachate. Moreover, since the concentration of formaldehyde in the sludge added to the cells was determined to be 1.6 ± 0.1 mg/ℓ, increases in leachate formaldehyde concentration were not due to the addition of sludge. The subsequent rapid decrease in the concentration of formaldehyde was attributable to the biodegradation of formaldehyde within the landfill cell. This removal of formaldehyde coincided with corresponding decreases in organic pollutants (COD, TOC, BOD_5) and increased gas production.

The estimated cumulative quantity of formaldehyde removed from the cell during the study period is presented in Table 23 and Figure 38.

Table 22. Formaldehyde Concentration of Leachate from Recycle and Single-Pass Cells

Sampling Day	Formaldehyde Concentration, mg/l	
	Recycle	Single- Pass
149	28.0 ± 2.4	22.4 ± 3.4
212	23.2 ± 2.4	18.0 ± 2.0
229	30.4 ± 1.6	18.6 ± 1.8
285	24.0 ± 2.5	9.2 ± 0.3
317	21.6 ± 2.0	18.4 ± 1.2
331	16.8 ± 0.8	16.1 ± 0.6
360	18.2 ± 3.6	23.8 ± 1.8
367	27.6 ± 1.6	-
388	36.2 ± 2.2	25.6 ± 0.6
397	41.8 ± 0.8	-
408	34.6 ± 1.4	28.6 ± 0.2
418	27.8 ± 1.6	15.0 ± 1.2
430	17.6 ± 2.4	16.2 ± 2.4
438	15.7 ± 0.6	-
460	7.6 ± 0.3	6.7 ± 0.1
468	-	3.8 ± 0.2
472	2.9 ± 0.2	-
491	3.1 ± 0.4	5.7 ± 0.5

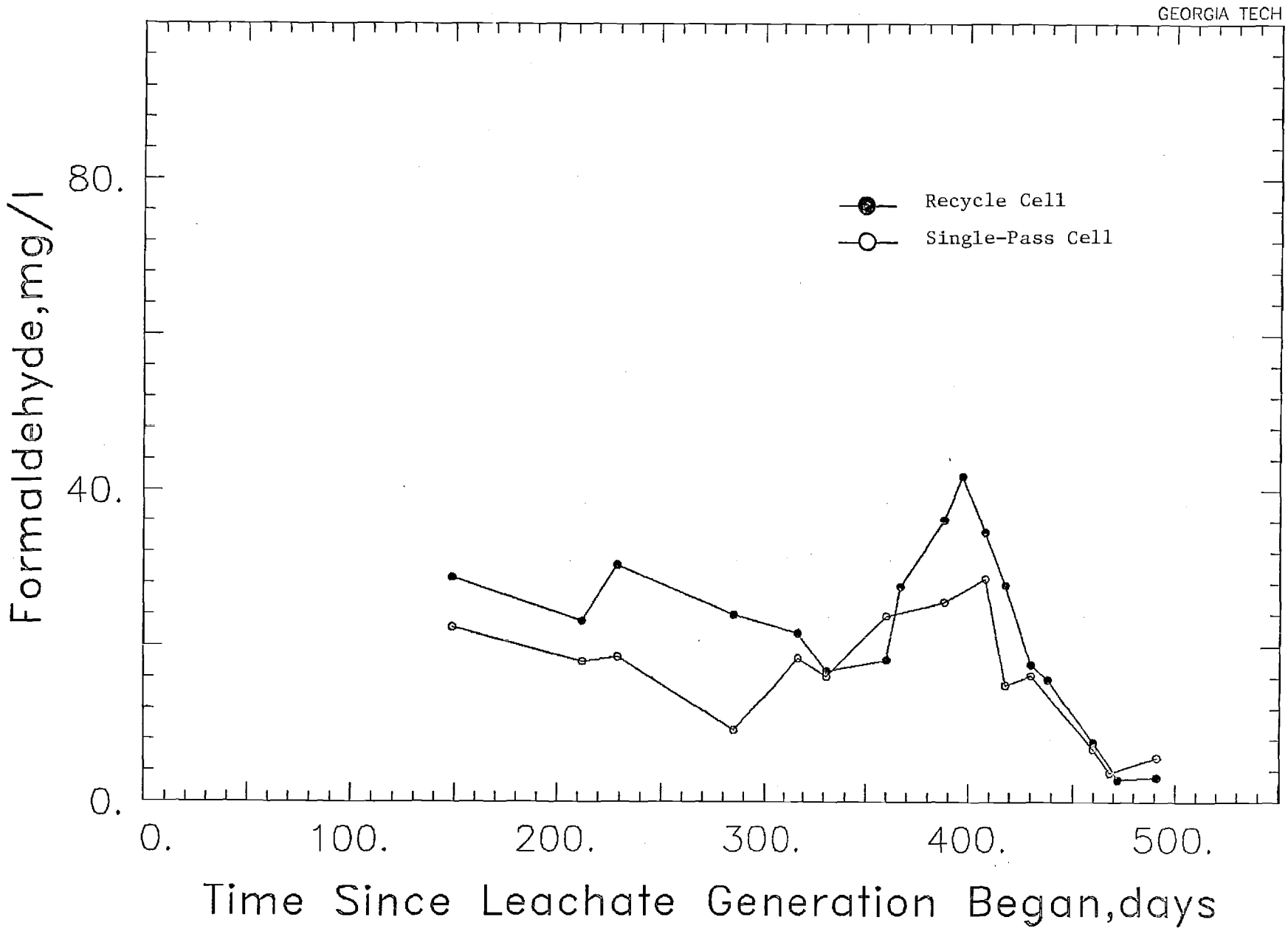


Figure 37. Concentration of Formaldehyde in Leachate

Table 23. Estimated Cumulative Amount of Formaldehyde Removed from Recycle Cell

Sampling Day	Leachate Removed Since Previous Sample, liters	Leachate Remaining in Cell, liters	Cumulative Amount of Formaldehyde Physically Removed from Cell, mg	Cumulative Amount of Formaldehyde Removed by Degradation, mg*	Cumulative Total Amount Removed, mg
149	13.0	34.1	364	-	364
212	3.5	30.6	445	-	445
229	1.0	29.6	476	-	476
285	3.5	26.1	560	-	560
317	1.5	24.6	592	-	592
331	1.0	23.6	609	-	609
360	4.0	29.6	682	-	682
367	2.0	27.6	737	-	737
368	3.0	24.6	845	-	845
397	3.0	21.6	971	-	971
408	1.0	20.6	1005	138	1144
418	0.5	20.1	1019	278	1298
430	1.0	19.1	1037	483	1520
438	0.5	18.6	1045	520	1564
460	1.0	17.6	1052	670	1723
472	0.75	16.35	1055	753	1808
491	1.0	15.35	1058	753	1811

*Assumes no degradation of formaldehyde occurred until maximum concentration was attained on Day 397.

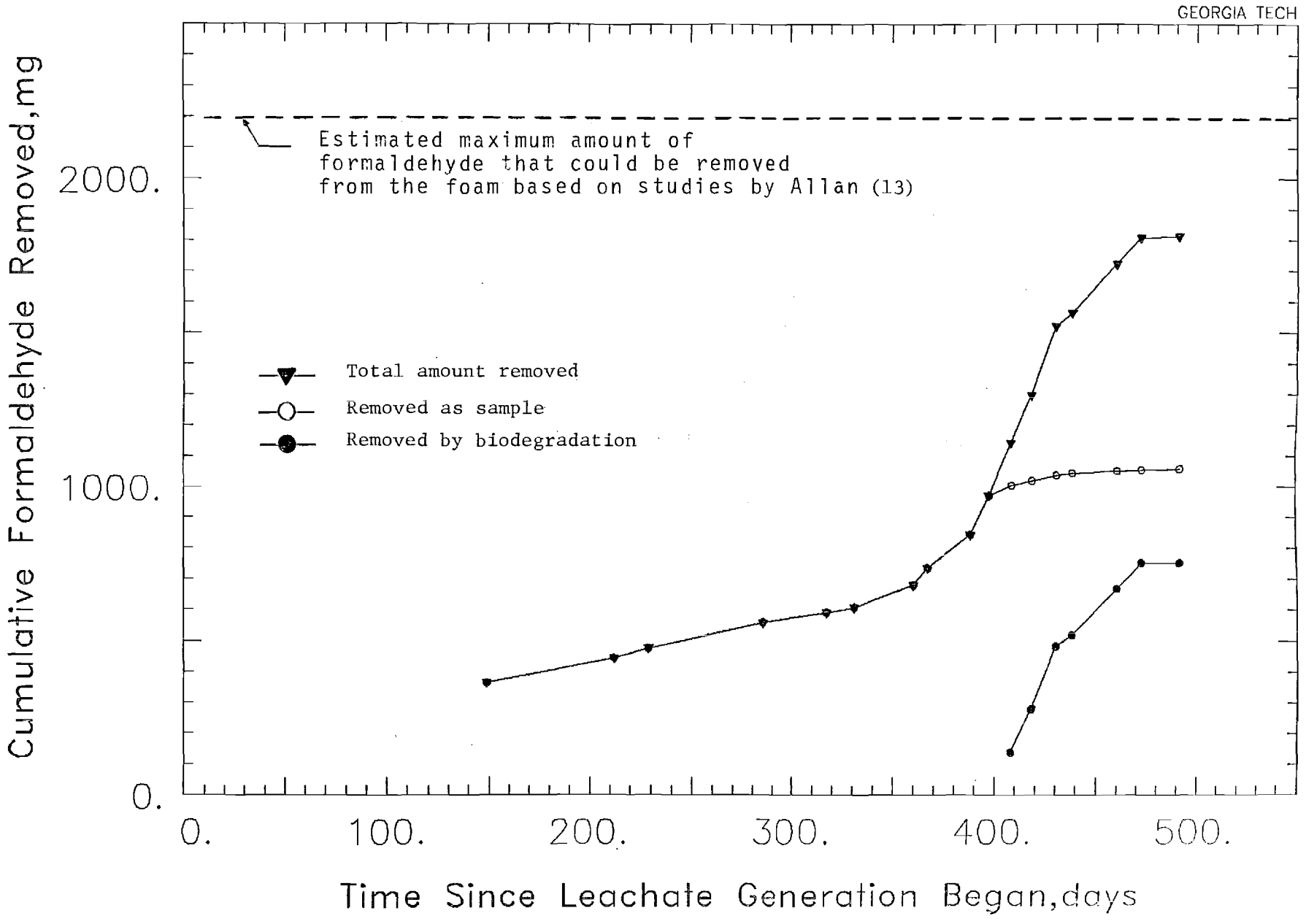


Figure 38. Estimated Cumulative Amount of Formaldehyde Removed from Recycle Cell

Removal of formaldehyde was attributable to either the physical removal of leachate from the cell for analysis or by degradation of the formaldehyde during landfill stabilization. Volatilization of formaldehyde from the leachate during recycle was not considered to be significant as formaldehyde is extremely soluble in water (40g/100 mℓ of water at 20°C).[12] These results indicated that a total of 1811 mg (16.5 mg/g of foam) were removed from the cell during the study period of which 753 mg(6.8 mg/g of foam) were attributable to biodegradation of the formaldehyde within the simulated landfill cell or 82.3% of the estimated maximum amount of formaldehyde (2200 mg) that potentially could be removed from the foam placed in the recycle cell, based on studies conducted by Allan.[13]

Formaldehyde concentrations in the single-pass cell ranged from 9.5 mg/ℓ to 28.6 mg/ℓ prior to decreasing to approximately 6 mg/ℓ on Day 491. The gradual increase in formaldehyde between Days 285 and 410 could be attributed to some tranformation of the foam within the cell and associated release of entrapped formaldehyde to the leachate; the subsequent decrease between Days 410 and 490 was due to wash-out of the residual amounts of formaldehyde remaining within the cell. Wash-out was considered to have been the primary removal mechanism for the formaldehyde from this cell as there was little indication that any significant stabilization had occurred within this cell. Therefore, assuming that wash-out was the major means of formaldehyde removal, a total quantity of 2025 mg (18.4 mg/g of foam) of formaldehyde was removed from this cell during the study period (Table 24 and Figure 39) which represents 92% of the estimated maximum amount that could be removed from the foam, based on the studies previously referenced.[13]

Table 24. Cumulative Amount of Formaldehyde Removed from Single-Pass Cell

Sampling Day	Leachate Removed from Cell Since Previous Sample, liters	Cumulative Amount of Formaldehyde Removed, mg
145	47.0	1053
210	7.0	1179
227	3.4	1254
285	7.0	1320
315	2.0	1356
360	18.8	1808
388	3.5	1899
410	2.5	1972
430	1.5	1994
460	3.5	2019
470	1.5	2025

A lesser quantity of formaldehyde was reported removed from the recycle cell (1811 mg) as compared with the single-pass cell (2025 mg). Although this difference might be attributable to possible differences in the quantity of foam placed in each cell as well as analytical error, assumptions made in the determination of the amount of formaldehyde removed from the cells may also account for this discrepancy. Moreover, in determination of the amount of formaldehyde removed, it was assumed that degradation of formaldehyde did not occur until the maximum concentration was reached on Day 397. This was approximately 40 days after the initiation of stabilization processes within the cell based on previously discussed organic pollutant concentration decreases and increased gas production. Therefore, some degradation of formaldehyde may also have occurred within the cell even as the concentration of formaldehyde was increasing due to the increased flushing of formaldehyde from the foam. If such degradation occurred, the total amount of formaldehyde removed from the cell would correspondingly increase.

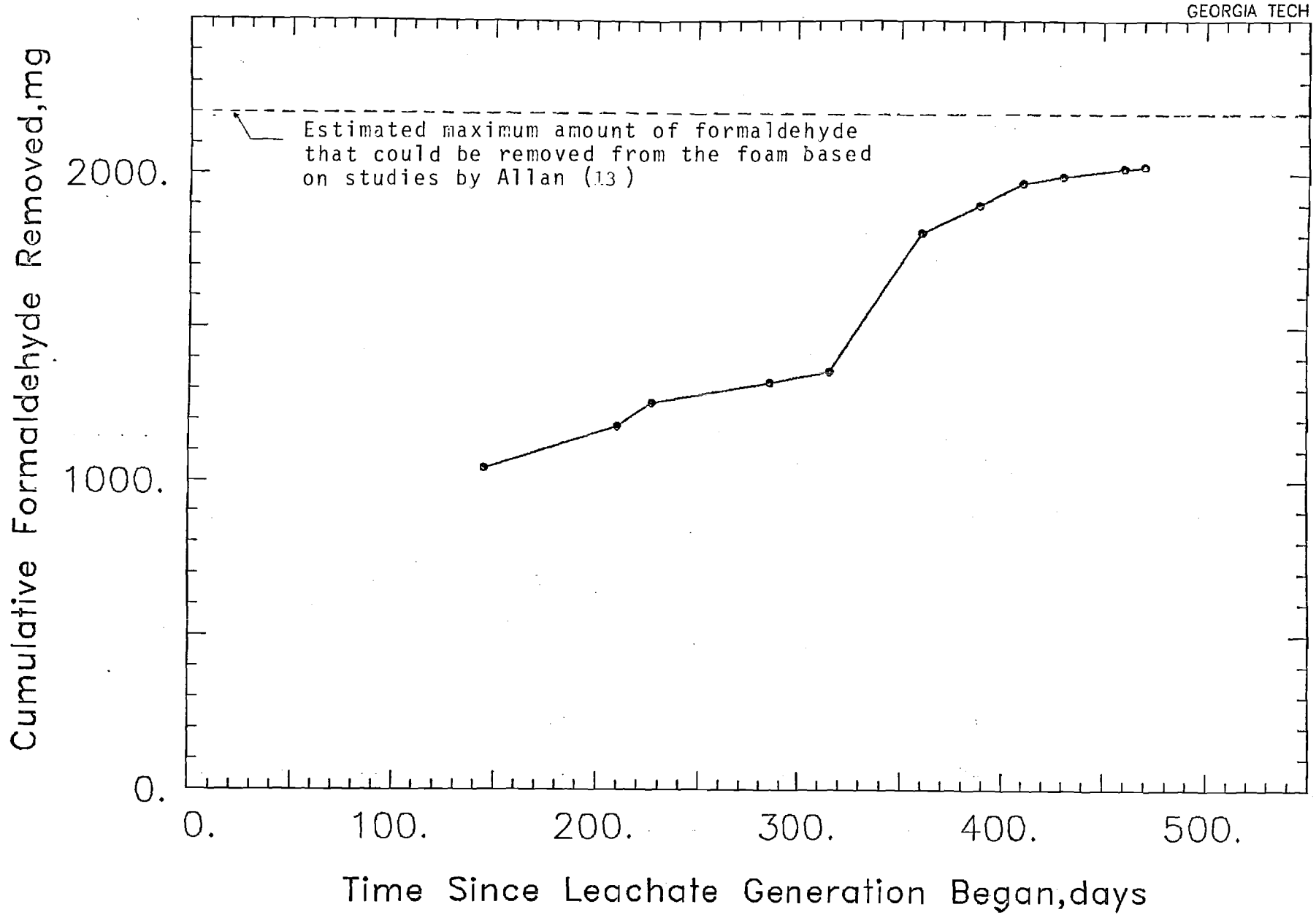


Figure 39. Cumulative Amount of Formaldehyde Removed from Single-Pass Cell

In an actual landfill, the amount of formaldehyde removed from the foam would be dependent on several factors including; thickness of the foam layer, moisture addition to the landfill, and opportunity for contact between the leachate and foam. All of these might vary significantly throughout the landfill and from site to site. Since the design and operation of the simulated landfill cells were conceived to insure the presence of moisture within the cells and the opportunity for contact between the leachate and the foam, the results obtained from these studies might be considered to reflect the maximum amount of formaldehyde that could be expected to be removed from foam within the landfill environment as expressed in terms of milligrams of formaldehyde removed/gram of foam.

The concentrations of formaldehyde measured during this study in both cells were much less than those that have been reported as being inhibitory to anaerobic degradation processes.[14] Indeed, inhibition to degradation processes were not observed once a viable methanogenic population was established within the cell. Furthermore, adverse health and environmental impacts as a result of the release of formaldehyde containing leachate to the environment are similarly remote. If such a leachate were to enter a ground water system, the relatively small quantity of formaldehyde present, the apparent opportunity for further degradation occurring in both the aqueous leachate medium and the hydro-geological setting, and the vast reservoir for high dilution capacity available in the ground water system would likely reduce its concentration below detectable limits. By comparison, concentrations of an average of 0.54 mg/kg and 8.2 mg/kg have been reported in beer and cola soft drinks, respectively.[15]

Leachability Tests - Bench-Scale Simulated Landfill Cells With and Without Foam

Data from tests conducted to determine if formaldehyde detected in landfill leachate was attributable only to the foam or also to other constituents of the solid waste are presented in Tables 25 through 28 and Figures 40 and 41. These data record the results of analyses performed on leachate samples to characterize the leachate generated by the cells and determine the quantity of formaldehyde removed from the cells.

Results of analyses performed on selected leachate samples from the cells containing only solid waste and containing solid waste with a one-inch (2.5-cm) foam layer are presented in Tables 25 and 26, respectively. These results indicate that the characteristics of the leachates generated by these cells were similiar and, hence, indicative of the presence of similar waste constituents and environmental conditions within both cells. In addition, the characteristics of these leachates were typical of leachates generated by sanitary landfills.[4]

Results of formaldehyde analyses performed on leachate samples collected subsequent to moisture additions to the cells at varying time intervals are presented in Tables 27 and 28 and Figure 40. These results indicate that low concentrations (1-2mg/ℓ) of formaldehyde were present in the leachate from the cell containing only shredded municipal waste (Table 27 and Figure 40). Therefore, formaldehyde necessarily originated from various constituents in the solid waste. This was not considered to be particularly unusual or unexpected, since there is widespread use of products containing formaldehyde-based resins (e.g., pressed wood products, insulation, paper, fabric,

Table 25. Analysis of Leachate from Bench-Scale Simulated Landfill Cell Containing Only Solid Waste

Sampling Date	Time, days+	Analytical Parameters					
		pH	COD, mg/ℓ	TOC, mg/ℓ	BOD_5, mg/ℓ	Alkalinity, mg/ℓ as $CaCO_3$*	Conductivity, μmhos/cm
11/27/82	12	5.02	20,000	5,000	5,200	3,375	4,200
12/03/82	29	4.94	22,400	6,200	8,800	-	-
02/11/83	88	5.13	24,800	7,600	11,000	6,875	8,100
02/27/83	104	5.22	33,600	10,600	13,000	7,125	8,000
04/05/83	141	4.93	24,400	7,400	21,500	5,150	-
04/22/83	158	4.82	24,900	6,500	22,000	3,700	-
06/09/83	206	4.85	26,300	7,100	-	-	-
07/05/83	232	4.88	24,000	7,700	-	5,450	-
08/26/83	284	5.90	25,500	9,000	-	9,500	-
11/01/83	357	5.48	-	5,800	-	5,250	-

*Titrated to pH 3.5.
+Since first moisture additions.

Table 26. Analysis of Leachate from Bench-Scale Simulated Landfill Cell Containing Solid Waste and Foam.

Sampling Date	Time, days+	Analytical Parameters					
		pH	COD, mg/ℓ	TOC, mg/ℓ	BOD, mg/ℓ	Alkalinity, mg/ℓ as $CaCO_3$*	Conductivity, μmhos/cm
11/27/82	12	5.15	21,000	5,800	7,400	3,188	5,500
12/03/82	29	4.90	21,600	6,200	9.400	-	-
02/11/83	88	5,38	36,000	11,000	14,500	7,250	5,700
02/27/83	104	5.41	38,400	11,200	13,800	7,500	7,800
04/05/83	141	4.90	24,100	7,400	22,000	4,700	-
04/22/83	158	5.05	24,400	6,700	23,500	5,000	-
06/09/83	206	5.06	26,350	6,900	26,350	-	-
07/05/83	232	5.07	27,770	7,000	-	5,000	-
08/26/83	284	5.97	24,700	8,800	-	7,800	-
11/01/83	357	5.50	-	7,400	-	6,050	-

*Titrated to pH 3.5.
+Since first moisture addition.

carpet),[4,5,16] many of which may eventually be disposed of in sanitary landfills. Since formaldehyde is extremely soluble in water, it could be readily extracted from these materials as field capacity was reached and leachate was generated within the landfill.

Table 27. Formaldehyde Concentration and Cumulative Amount of Formaldehyde Removed from Bench-Scale Simulated Landfill Cell Containing Only Solid Waste

Sampling Date	Time, days*	Formaldehyde Concentration of Leachate, mg/ℓ	Cumulative Volume of Leachate Removed from Cell, liters	Cumulative Amount of Formaldehyde Removed from Cell, mg
11/29/82	14	1.0	0.60	0.60
12/03/82	29	1.0	0.93	0.93
12/19/83	45	1.0	1.23	1.23
02/11/83	87	0.9	1.58	1.55
02/27/83	104	1.3	1.78	1.81
03/18/83	123	1.4	1.98	2.09
04/05/83	141	0.6	2.38	2.33
04/22/83	158	0.4	3.18	2.61
05/08/83	172	0.6	4.13	2.94
06/08/83	205	0.6	4.73	3.60
08/10/83	268	2.0	6.68	6.60
08/26/83	284	2.0	7.58	8.40
11/01/83	357	1.4	10.43	11.97

*Since first moisture addition.

Formaldehyde concentrations in the leachate from the cell containing a 1-inch(0.5-cm) layer of foam ranged from 1.5 to 3.0 mg/ℓ during the initial phase of the test (Day 14 to Day 158; Table 28 and Figure 40). This was slightly greater than the concentration measured in the cell containing only solid waste and could be attributed to the leaching of formaldehyde from the foam. The small amount of formaldehyde removed during this period (0.8 mg/g of foam) indicated that there did not appear to have been an initial flushing of formaldehyde from the foam.

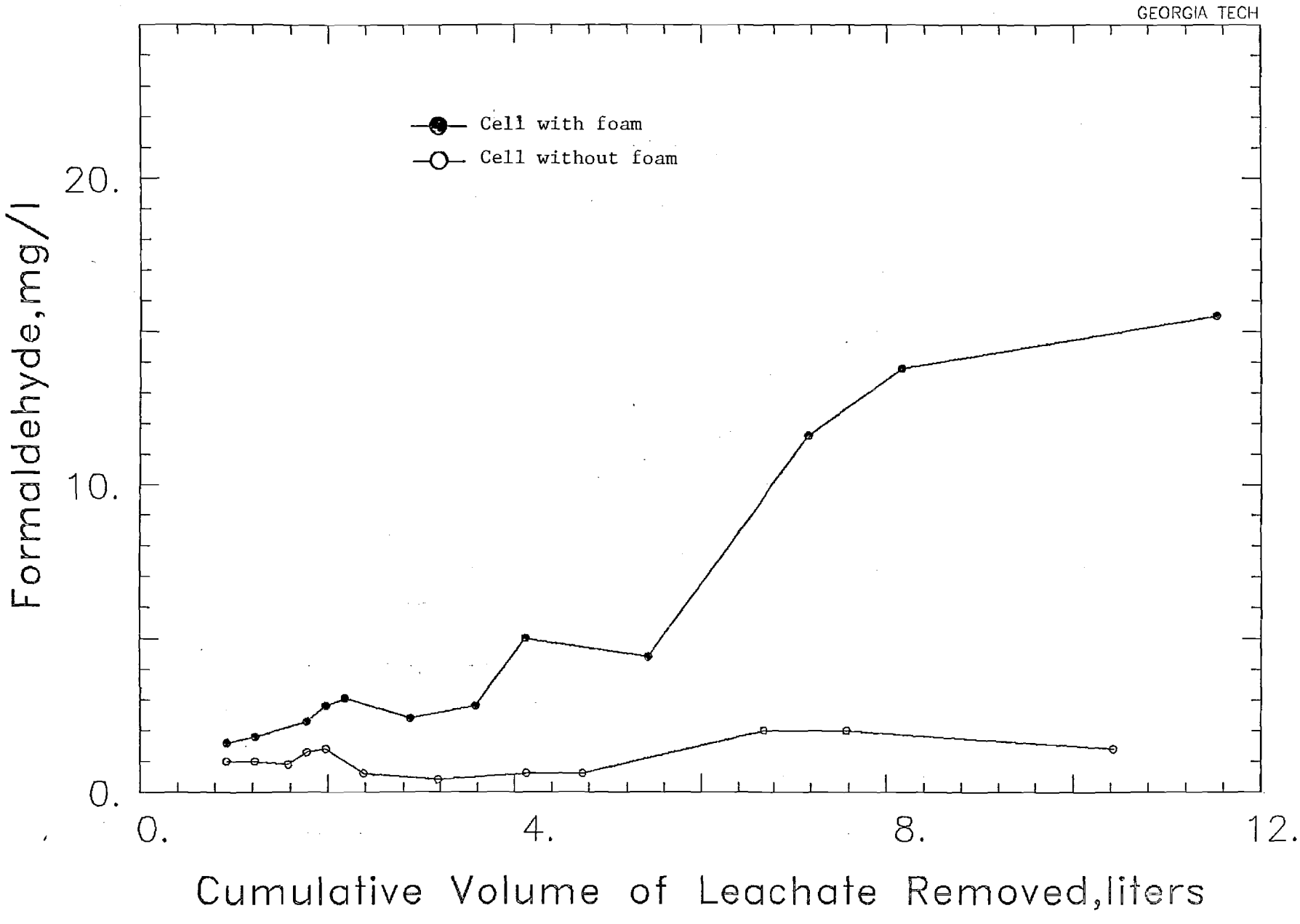


Figure 40. Concentration of Formaldehyde Removed from Leachate from Bench-Scale Simulated Landfill Cells With and Without Foam

Table 28. Formaldehyde Concentration and Cumulative Amount of Formaldehyde Removed from Bench-Scale Simulated Landfill Cell Containing Solid Waste and Foam

Sampling Date	Time days*	Formaldehyde Concentration of Leachate, mg/ℓ	Cumulative Volume of Leachate Removed from Cell, liters	Cumulative Amount of Formaldehyde Removed from Cell, mg
11/29/82	14	1.6	0.60	0.96
12/03/82	29	1.6	0.93	1.48
12/19/82	45	1.8	1.23	2.02
02/11/83	87	2.3	1.78	3.28
02/27/83	104	2.8	1.98	3.84
03/18/83	123	3.04	2.18	4.45
04/05/83	141	2.4	2.88	6.13
04/22/83	158	2.8	3.58	8.09
05/08/83	172	5.0	4.13	10.84
06/08/83	205	4.4	5.43	16.56
08/10/83	268	11.6	7.18	36.86
08/26/83	284	13.8	8.18	50.66
11/01/83	357	15.5	11.53	96.40

*Since first moisture addition.

However, subsequent leachate samples over extended time intervals indicated an increase in the concentration of formaldehyde present in the leachate removed from the cell. (A similiar trend was demonstrated previously for the single-pass simulated landfill cell where the gradual degradation of the foam within the cell led to the subsequent release of formaldehyde.)

The cumulative amounts of formaldehyde removed from the cell

containing only solid waste and that containing both solid waste and foam are also presented in Tables 27 and 28 and in Figure 41. A total of approximately 12mg (3.1 mg/dry kg of solid waste) were removed from the cell containing only solid waste, whereas, approximately 96 mg (24.6 mg/dry kg of solid waste) were removed from the cell containing the foam. This corresponded to approximately 9.6 mg/g of foam placed in the cell. Consequently, although the solid waste placed in the cells contained constituents capable of releasing formaldehyde to the leachate, additional quantities of formaldehyde were also extracted from the foam placed within the cell.

Considering that a much smaller ratio of foam to solid waste would prevail in an actual landfill setting (i.e., about 1.7 percent for a 3.0-m (10-ft) lift as compared to 8 percent for the simulated 0.6-m (2-ft) landfill cells), and assuming that similar extractions of formaldehyde from constituents present in the solid waste occurred, approximately 25 percent of the total mass of formaldehyde leached from the landfill cell could be attributed to the solid waste.

Anaerobic Digestibility Studies

Data from the digestibility studies conducted to determine the degradability of formaldehyde under anaerobic conditions and the possible inhibition to biodegradation attributable to constituents contributed by the foam to the leachate are presented in Tables 29 through 32 and Figures 42 and 43. The time scale used in these figures corresponds to the number of days since start-up of the batch digestors.

Comparison of the composition of the leachate as a substrate (Table 29) with the supernatant from this digestor (Table 30) indicates

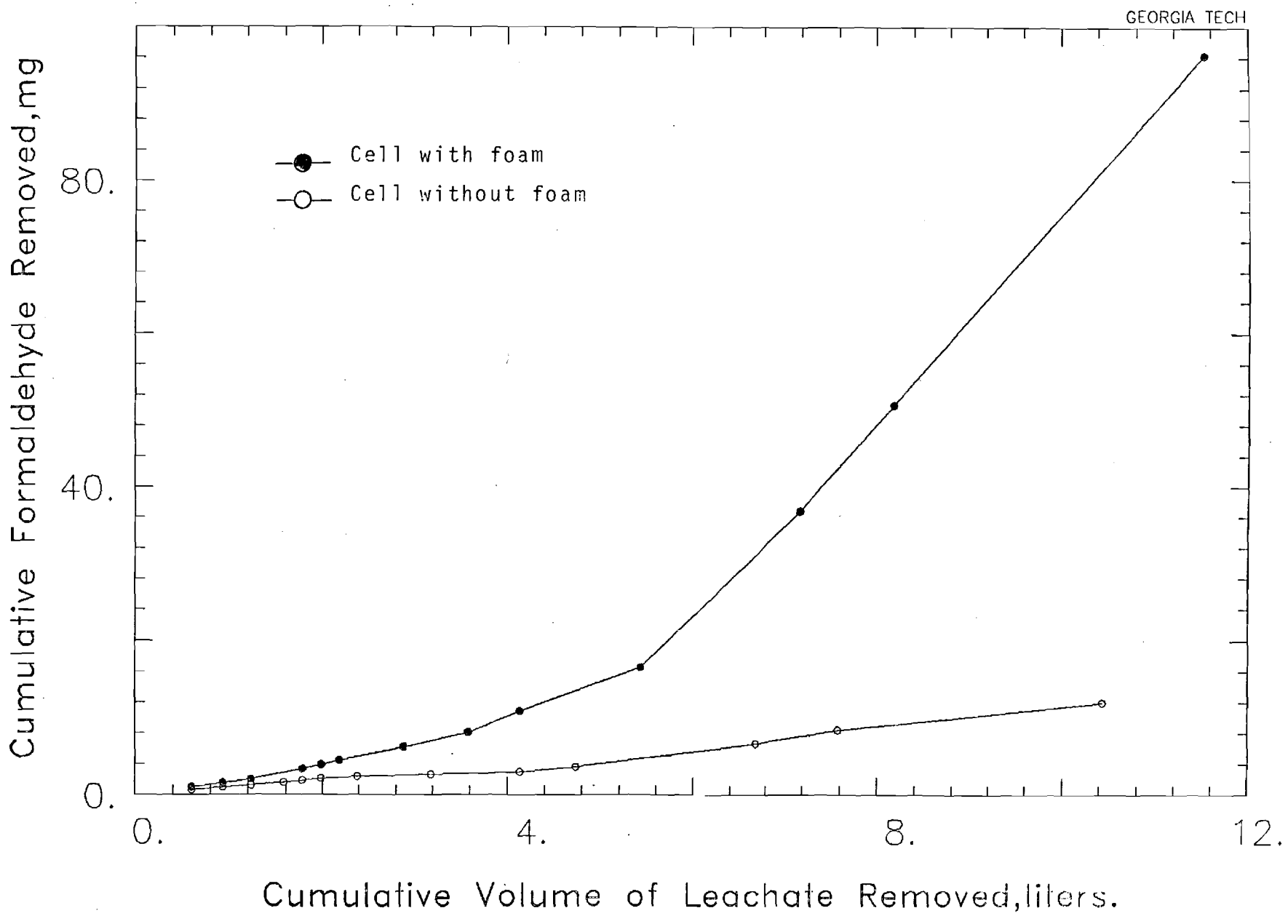


Figure 41. Cumulative Amounts of Formaldehyde Removed from Bench-Scale Simulated Landfill Cells With and Without Foam

Table 29. Characterization of Leachate Added to Digestor as Substrate

Sampling Day	Analytical Parameter						
	pH	ORP, mV E_c	Conductivity, µmhos/cm	Alkalinity, mg/ℓ as $CaCO_3$*	COD, mg/ℓ	TOC, mg/ℓ	Formaldehyde, mg/ℓ
6**	5.11	-72	8,900	6,250	21,000	7,800	-
35**	5.19	-68	8,400	5,300	18,000	7,200	25.6
71	5.09	-	12,000	6,500	43,000	14,225	-
85	-	-	-	-	-	-	13.0
143	5.11	-	11,500	6,300	39,000	-	-

*Titrated to pH 3.5.
**Acclimation period.

Table 30. Characterization of Digestor Supernatant

Sampling Day	Analytical Parameter						
	pH	ORP, mV E_c	Conductivity, µmhos/cm	Alkalinity, mg/ℓ as $CaCO_3$*	COD, mg/ℓ	TOC, mg/ℓ	Formaldehyde, mg/ℓ
6**	7.12	-250	-	4,700	24,000	-	-
40**	-	-	-	-	-	-	6.6
66	7.04	-270	10,600	5,950	3,400	2,600	-
85	7.07	-265	10,500	6,150	8,280	7,590	-
143	7.05	-260	-	6,550	6,500	5,850	4.0

*Titrated to pH 3.5.
**Acclimation period.

that COD removal of approximately 82% was achieved during steady-state operation of the digestor. Furthermore, formaldehyde reductions ranged from 75% on Day 140 to 70% on Day 143. Hence, the formaldehyde present in the leachate was being biodegraded under anaerobic conditions as volatilization of formaldehyde was considered unlikely due to its high solubility.

Digestor loading rates and cumulative gas production rates are presented in Table 31 and Figure 42. The digestor which received no additional substrate addition produced a total of 1.952 liters of gas. This was attributable to the continual degradation of biodegradable organic matter present in the seed sludge. The composition of the gas generated (Table 32) indicated that, although anaerobic decomposition was occurring, the quantity of gas produced was insufficient to completely flush out the air that had been introduced into the digestor during start-up.

The digestor which received leachate as a substrate was acclimated to the leachate by gradually increased loadings from 0.49 to 0.98 g COD/ℓ·d during the first 75 days of the study (Table 32). The loadings were then increased to approximately 2 g COD/ℓ·d for the duration of the study. Gas production increased with increased loadings and, subsequent to the acclimation phase, remained constant (Figure 42). The gas composition from this digestor, presented in Table 33 and Figure 43, also remained relatively consistent throughout the study period. Since no lag in gas production was observed when leachate was initially added to the digester and good removal of COD with a corresponding constant rate of gas production was attained, constituents inhibitory to anaerobic degradation did not

Table 31. Digestor Loadings and Cumulative Gas Production

Day	Digestor Receiving Leachate as Substrate		Digestor Without Substrate Addition
	Average Loading, gm COD/ℓ·d	Cumulative Gas Production, liters @ STP	Cumulative Gas Production, liters @ STP
1	0.49	0	0.342
5	0.49	3.35	1.347
10	0.49	6.64	1.724
15	0.25	8.17	1.952
20	0.29	9.43	-*
25	0.29	10.62	
30	0.59	13.58	
35	0.78	16.64	
40	0.98	19.92	
45	0.78	23.14	
50	0.78	25.77	
55	0.98	32.62	
60	0.59	33.13	
65	0.98	35.99	
70	0.98	39.41	
75	2.06	44.61	
80	2.06	52.53	
85	2.06	59.67	
90	1.73	65.40	
95	1.73	71.98	
100	2.06	80.20	
105	2.06	85.36	
110	2.06	93.24	
115	1.89	100.94	
120	2.22	107.95	
125	1.75	116.14	
130	1.65	125.13	
135	2.06	134.03	
140	2.06	141.24	
145	2.06	149.93	

*Measurable Gas Production Ceased.

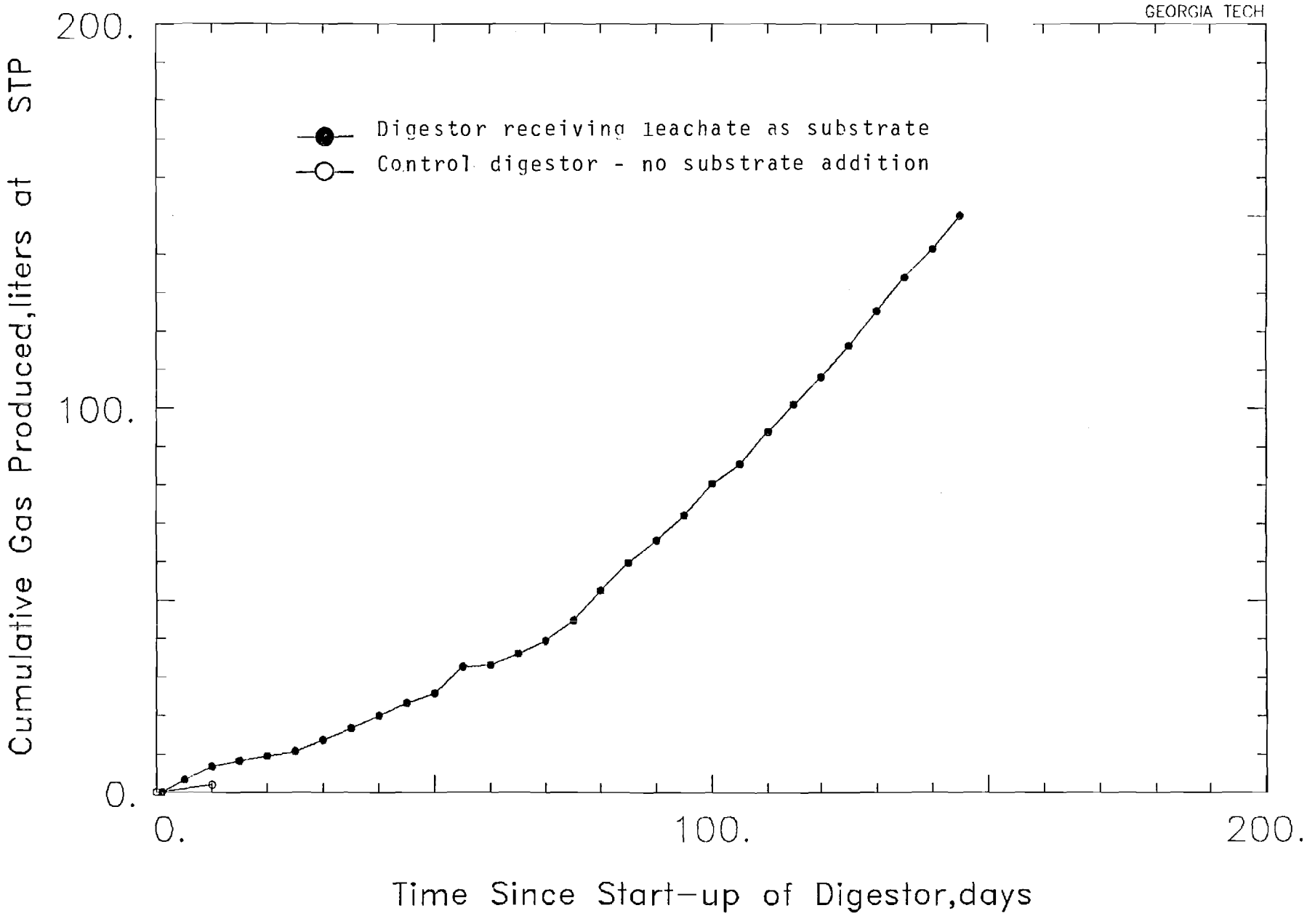


Figure 42. Cumulative Gas Production from Batch Digestors

Table 32. Gas Production from Batch Digestors

Sampling Day	Composition of Gas from Digestor Receiving Leachate, %					Composition of Gas from Digestor Without Leachate Addition, %				
	N_2	CO_2	O_2	H_2	CH_4	N_2	CO_2	O_2	H_2	CH_4
6	5	27	<1	-*	68	21	17	3	-	59
8	5	27	<1	-	68	22	19	4	-	55
13	5	27	<1	-	68	23	19	3	-	54
16	4	26	<1	-	68	16	21	2	-	61
20	3	27	<1	-	70					
26	7	28	-*	-	65	(Measurable Gas Production Ceased)				
30	4	29	-	-	67					
33	2	30	-	-	68					
37	3	30	-	-	67					
41	3	30	-	-	67					
51	3	30	-	-	67					
57	3	28	-	-	69					
65	3	29	-	-	68					
70	3	30	-	-	67					
76	1	30	-	-	69					
83	1	27	-	-	72					
89	<1	25	-	-	74					
106	4	28	-	-	68					
114	4	27	-	-	69					
126	2	28	-	-	70					
141	5	30	-	-	65					

*Not Detected.

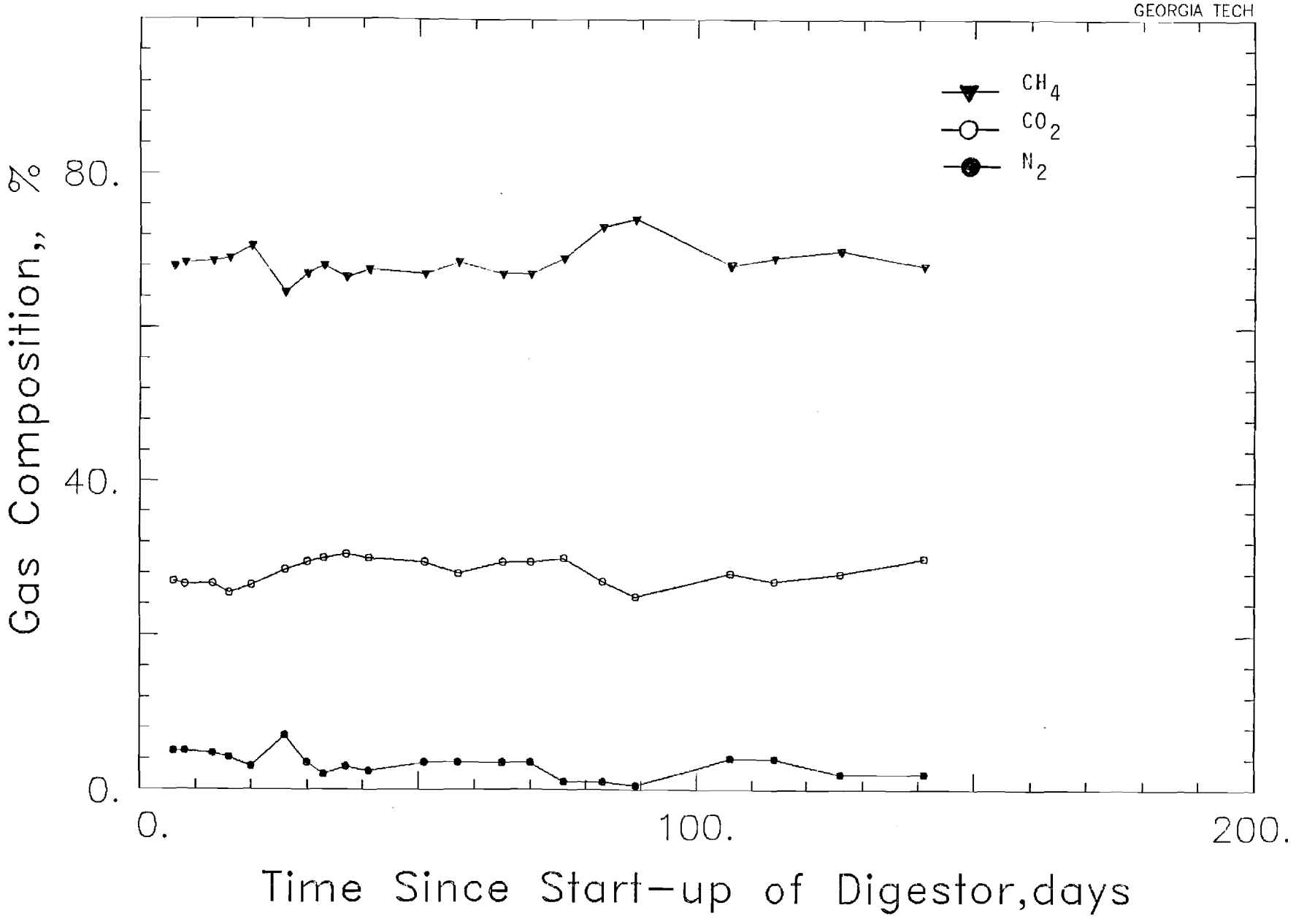


Figure 43. Composition of Gas from Batch Digestor Receiving Leachate Substrate

appear to be present in the leachate during the period when formaldehyde concentrations were present.

SUMMARY AND CONCLUSIONS

From the results of the research investigations, the following summary and conclusions can be presented.

1. Derivatization of formaldehyde as 2,4-dinitrophenylhydrazone was developed as a reliable method for determination of formaldehyde in leachate and, therefore, is recommended for monitoring of leachate and other similarly complex aqueous solutions for formaldehyde.

2. Under the conditions of experiments simulating conventional landfill management both with and without recycle, the total masses of formaldehyde removed from the simulated landfill cells containing 2.8 g of foam/dry kg of solid waste were determined to be 16.5 and 18.4 mg/g of foam, respectively, over the 500-day study period.

3. Some of the formaldehyde detected in the leachate from the simulated landfill cells (approximately 3 mg/dry kg of solid waste) originated from the solid waste itself. With similar removals of formaldehyde from solid waste in an actual landfill, approximately 25% of the total mass of formaldehyde leached from conventional landfill cells covered with foam could originate from the solid waste.

4. Formaldehyde and possible other constituents leached from the foam in the simulated landfill cells did not preclude anaerobic microbial production of methane during landfill stabilization.

5. Formaldehyde concentrations in the leachate from the recycle simulated landfill cell were decreased from a high of 41.8 mg/ℓ to less than 3 mg/ℓ during the methane fermentation phase of landfill stabilization. This removal was accelerated by utilizing leachate containment,

collection, and recycle as an *in situ* treatment method.

6. SaniFoam plastic foam may be used as an alternative to daily landfill cover without posing adverse environmental impacts attributable to the release of formaldehyde from the foam.

APPENDIX A

ANALYTICAL METHODS FOR THE DETERMINATION OF FORMALDEHYDE IN AQUEOUS SOLUTIONS

A. Chromatropic Acid Method for the Determination of Formaldehyde in Aqueous Solutions[17]

1. Reagent Preparation: Dissolve 2.5 g of dry powdered chromatropic acid in 25 ml of distilled water and filter to obtain a clear solution.

2. Procedure:

   a) Place 0.5 ml of sample in a 50-ml glass stoppered volumetric flask.

   b) Add 0.5 ml of chromatropic acid reagent followed by the gradual addition of 5 ml of concentrated sulfuric acid with continuous shaking.

   c) Stopper flask and place in boiling water for 30 minutes. Cool and dilute to 50 ml, cool again and readjust volume to 50 ml if necessary.

   d) Read adsorbance on a spectrophotometer at a wavelength of 570 millimicrons.

B. Gas Chromatographic Method for Determination of Formaldehyde in Aqueous Solutions

1. Instrument: Perkin Elmer Sigma 3.

2. Experimental Conditions:

   a) Injection mode; on column

   b) Injector temperature; 250°C

   c) Column; 1) Porapax G 60/80 mesh
      2) Porapax T 60/80 mesh, glass column 1.83 m long, 2 mm I.D.

   d) Oven Temperature Program; 130°C (5 min), 5°/Min → 150°C (1 min)

   e) Volume Sample Injected: 1.0 microliter

C. Gas Chromatographic-Mass Spectroscopy (GC-MS) Method for Determination of Formaldehyde in Aqueous Solutions

1. Instrument (GC): Hewlett Packard 5830 A GC

2. Experimental Conditions (GC):

   a) Injection mode; split mode (split ratio 50:1)

   b) Injector temperature; 250°C

   c) Column; glass capillary 30 m x 0.35 mm I.D., carbowax 20 M

   d) Oven Temperature Program; 40°C (0.2 min), 20°C/min → 230°C

   e) Volume Sample Injected; 1.0 microliter

   f) Transfer Line; fused silica tubing 0.2 mm I.D.

3. Instrument (MS): Finnigan 4023 MS and Nova 3 Data System

4. Experimental Conditions (MS):

   a) Ionization Mode; Electron Impact

   b) Electron Energy; 70 eV

   c) Emission Current; 0.5 mA

   d) Electron Multiplier; 1450 V

   e) Multiple Ion Detection; m/e 29 and 30

APPENDIX B

2,4-DINITROPHENYLHYDRAZONE (DNPH) DERIVATIVE METHOD FOR THE DETERMINATION OF TRACE AMOUNTS OF FORMALDEHYDE

1. Reagent Preparation:

   Dissolve 0.25 g of 2,4-dinitrophenylhydrazine (DNP) in 100 ml of 6 M hydrochloric acid.[8]

2. Glassware Preparation:

   All glassware must be cleaned and prepared by the standard techniques used for trace organic analysis (i.e. soap and water wash, "organic-free" water rinse and baked overnight at 500°C).

3. Procedure:

   a) To 100 ml of sample, add 5 ml of DNP reagent.

   b) Mix the sample with a magnetic stirrer for 5 minutes and then add 50 ml of methylene chloride.

   c) Continue mixing for 1.5 hours.

   d) Place the solution in a separatory funnel and separate the organic solvent from the aqueous solution.

   e) Perform the extraction two more times with 50-ml aliquots of methylene chloride.

   f) Concentrate the organic solvent to approximately 4 ml with a Kuderna-Danish apparatus at 70°C and finally to 1 to 1.5 ml by gentle drying with nitrogen.

   g) Analyze the sample by gas chromatography.

4. Gas Chromatographic Conditions:

   a) Instrument; Hewlett Packard 5830A equipped with capillary injection port.

   b) Injection Mode; splitless.

   c) Injector Temperature; 250°C.

d) Column; glass capillary, 0.3 mm I.D., 30 m long coated with SE-54.

e) Oven Temperature Program; 40^{o}C (2.0 min), 15^{o}/min for 6 minutes, 6^{o}/min for 8 minutes, 15^{o}/min for 4 minutes, 290^{o}C (5 min).

f. Volume Sample Injected; 0.5 microliter.

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